"Ozon" in Blue Discharge (Display Sign).

OZONE

ITS MANUFACTURE, PROPERTIES

AND USES

BY

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75 ILLUSTRATIONS

1106

To

Felix Louis Ortt
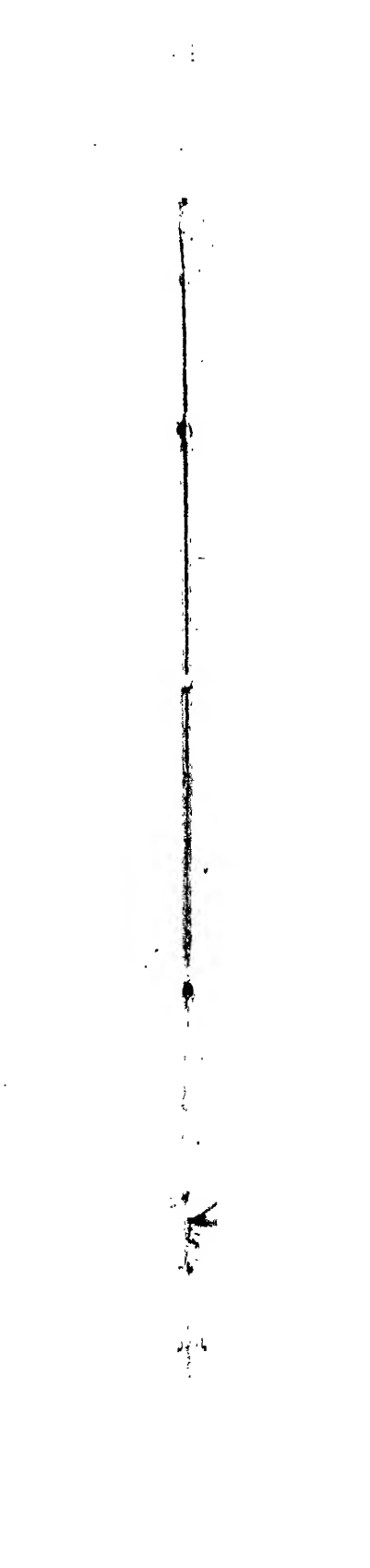
My Friend and Collaborator

This Book is Dedicated

PREFACE

The present volume gives the results of the author's investigations and experience with ozone extending over a period of some fifteen years. This experience has often led him to form different opinions from those commonly held on this subject. He has not hesitated to give these opinions frankly, believing that this is the best way to promote progress in a scientific field.

The subject of ozone is one of great variety; it is on the boundary of technics and science, involving chemistry, physics, bacteriology, hygiene, industrial chemistry, electrical and mechanical engineering. This book is intended to be a guide for those interested in the subject of ozone. Descriptions of plants have appeared now and then in different periodicals, and it seemed superfluous to include such material here, therefore we have referred to them only briefly. Our main object was to give a full outline of our personal experience and that same experience has made us very critical about outside information. There are very many publications on Ozone that cannot be classed otherwise than as commercial information and advertising matter. If a reader desires that, he might write to the various companies for pamphlets. The rather lengthy discussion on brush discharge is due to the fact that there are hardly any publications at all on this particular subject, and it may be that within a reasonable time the brush discharge will be used to accomplish many more reactions than just converting oxygen into ozone, its possibilities having been as yet very little investigated, though publications have been given here and there.

<div align="right">A. Vosmaer.</div>

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PART I

NATURE OF OZONE

CHAPTER I

EARLY HISTORY OF OZONE

THE early history of ozone is of little interest. It was discovered (or rather observed) by van Marum in 1785, who called attention to the peculiar odor developed by his static machine. As this apparatus was a very large one (conserved in Teyler's museum, Haarlem, Holland), he probably obtained considerable ozone.

The presence of one part of ozone in a million parts of air is easily perceptible, so when someone detects, say, ten times as much, we can hardly call it a discovery.

Van Marum noticed a considerable contraction of volume of oxygen when it was subjected to the discharges of his machine. This contraction was due to the oxidation of the mercury over which the oxygen was being kept; he also noticed the formation of red oxide of mercury.

In 1801 Cruikshank observed that when water is decomposed electrolytically, the resulting oxygen possesses a very peculiar smell, of which he did not know the cause. Not until 1840 was there any new discovery regarding ozone, but in that year Schoenbein made some observations about the odor and oxidizing properties of the ozone generated when water was electrolyzed or air was electrified. He gave the name of " ozone " to the

new gas because of its peculiar strong smell (after the Greek word "ozein," which means "to smell"); but, of course, did not know then what it was, and tentatively tried all sorts of hypotheses. Physical annals of that time contain minute details about all the "facts" which are now classified as mistakes or wrong explanations, a repetition of which would be of little use here.

For those interested in the history we refer to the work of C. Engler, published in 1870, and called: "Historisch-Kritische Studien über das Ozon." In our days of excessive literature there is no time for the consideration of obsolete speculations about the nature of a substance; it is quite enough to read established facts, hence we may pass over those ancient publications and speculations about ozone being a nitrogen or a hydrogen compound, etc.

When it was generally admitted that ozone was some kind of oxygen, there still was doubt about the simultaneous existence of "antozone." This antozone theory was supported by many people and Fox wrote a large volume entitled "Ozone and Antozone"; antozone later on was definitely proved to be nothing else but peroxide of hydrogen.[1]

Ozone was recognized as active oxygen, but it has taken many years to get rid of the misinterpretations of its specific behavior.

It was not until the year 1865 that Soret settled the question; and finally most investigators agreed that ozone is a tri-atomic oxygen.

Even now we are not wholly in unanimity on the subject of the constitution of ozone, but in order to avoid all difficulty beforehand, we wish to say that as long as opinions differ as to the true constitution of ozone we, in the meantime, will reverse the question, that is, we do not say ozone is O_3, but we say O_3 is ozone, that leaves the opportunity of giving other names to such compounds as O_4 or O_6, etc.

1. Now again the name antozone is sometimes used anew, not for the H_2O_2, but for an atomic or ionic oxygen liberated from ozone.

CHAPTER II

CONSTITUTION OF OZONE

RECENTLY J. J. Thomson[1] showed that we have at least nine different substances when a discharge passes through oxygen gas, namely:

1. Neutral molecular oxygen;
2. Neutral atomic oxygen;
3. Atomic oxygen with one positive electric charge;
4. Atomic oxygen with two positive charges;
5. Atomic oxygen with one negative charge;
6. Molecular oxygen with one positive charge;
7. Ozone with one positive charge;
8. Polymerized oxygen with one positive charge;
9. Free corpuscles.

Harries[2] states that ozone sometimes contains a considerable amount of O_4, to the extent of one-third or more; there will always be uncertainty about it, as long as the gas that we call ozone for the sake of brevity is really oxygen containing more or less ozone, and generally less, for it requires very special means to separate those two entirely.

When strongly ozonized oxygen is liquefied and the product subjected to fractional distillation, it appears to be possible to obtain an 86 per cent ozone.[3] When liquid ozone is evaporated, the resulting gas is not pure ozone either. It is probable that in the near future the conditions of equilibrium of the system ozone-oxygen will be taken up by some able investigator and that will probably throw some more light on the subject. For the present moment there is ample space for speculation, the system being very unstable indeed.

1. Chem. News, 1911, p. 265.
2. Ibid., p. 299.
3. Ladenberg, Ber. d. Chem. Ges., 1898, V. 31, p. 2508.

Another difficulty is the graphic formula; is it O—O or $O\!\equiv\!O$?
$$\underset{O}{\diagdown\!\diagup}\qquad\underset{O}{\diagdown\!\diagup}$$

Objection has been raised to the original and more simple O—O because all atoms would be of the same value and the
$$\underset{O}{\diagdown\!\diagup}$$
equality suggests a strong substance rather than an unstable one. The case is different with $O\!\equiv\!O$, because this explains
$$\underset{O}{\diagdown\!\diagup}$$
the liability to loose an atom, one of them being in a different position from the other two.[1]

This latter view implies the acceptance of the old opinion that ozone, when it has performed its function, returns to its original form of oxygen. We have to consider ozone, then, as a molecule of oxygen with an atom of O attached. This atom, difficult to attach, is easily let loose, hence its great oxidizing power. Thus we have oxygen in *statu nascendi* when applying ozone in processes of oxidation.

We do not believe in this theory, but incline to the old formula O—O, thereby admitting that when triatomic O_3 does
$$\underset{O}{\diagdown\!\diagup}$$
its work, it will yield three atoms of O.

Recently it has been proved that in the case of the oxidation of stannous chloride the O_3 gives us three O atoms. Yoshito Yamanchi,[2] who observed this, added, however, that in other cases the usual splitting up in O_2 and O occurs. We do not share this latter opinion, for reasons given later.

It seems probable, however, that the old way of viewing ozone as a modification of oxygen will have to give way to the more logical interpretation that pure ozone is a definite substance itself, O_3, and the commercial gas a mixture of O_2 and O_3 in first instance, possibly with O_4 or O_6 present as well. Instead of concluding that as there is dissimilarity between the ozone atoms, their bonds must be unsymmetrical, we prefer the view that all atoms of ozone are alike, hence there is

1. Mellor, Inorganic Chemistry, p. 191.
2. Eng. News, 1913, II, 99.

probably a similarity in the binding to $O\diagdown\!\!\begin{smallmatrix}O\\ |\\ O\end{smallmatrix}$. Logical reasoning will do more to elucidate this problem than actual experiment as long as we cannot produce pure ozone.

   Valency, and more so the variable valency, is not a clear subject either, and it is hard to understand why ozone should not be a true substance instead of oxygen with some appendix.

CHAPTER III

NATURE OF OZONE

THERE is a general tendency to explain the nature of a new substance by comparing it with some other which is already more familiar.

When van Marum first noticed the peculiar smell he compared it to the smell of sulphur; later he thought it more like chlorine. Schoenbein also mentions the smell of phosphorus or garlic. Now chemists will have to admit that if something smells like sulphur, or like chlorine, or like phosphorus, or like garlic, it will probably not be like any of these; moreover an odor is very hard to describe or compare, and the best we can do is to say that ozone smells like ozone and not expect it to be like something else. It is so definite and strong that it really is entitled to be considered an individual smell.

That same feeling toward comparison has occasioned many a wrong name. Some people speak of electrified oxygen, others of activated oxygen, some call it polymerized oxygen and the name of condensed oxygen has also been used; none of these names suit the purpose; electrified oxygen is quite another thing. The "molecular O_2 with one positive charge" of Thomson (see p. 3), seems to come up to that qualification; activated oxygen is not the right name either; this probably is O_2 mixed with atomic O; that question is not settled yet. The name polymerized or condensed should be reserved for the O_4 and O_6 modifications, and that leaves for ozone just the word ozone; there is no need for another, and it covers its odor at the same time.

To conclude this chapter on the nature of ozone we may say that for the present moment we are on the safe side if we consider ozone to be O_3. The recent work of Ladenburg has shown and definitely confirmed the fact that the molecule of ozone consists of an aggregate of three atoms of O.[1] It seems very

1. Molinari. Inorganic Chemistry, 1912.

probable that the bonding will be the symmetrical O—O and

$$\underset{O}{\diagdown\diagup}$$

that, when splitting up, ozone will produce three atoms of O, some of which may occasionally combine to form oxygen, these being lost from an economic standpoint.

Within a short time we will have to have separate names for substances in their molecular and in their atomic states, now having but one name, there being always the danger of forgetting to discriminate sharply between the two. 'In physics we are used to handling molecules and molecular properties; in chemistry the atom and the atomic properties are the more important; in fact we may call chemistry atomic physics, the essential difference between chemistry and physics being in the rôle played by stoichiometry, and this depends on atoms, not on molecules.

What makes ozone such a wonderful oxidizing agent? Is it the fact that in ozone we have a substance yielding oxygen in *statu nascendi* or atomic state?

We are quite familiar with this state for hydrogen, and know how absolutely differently hydrogen acts when in that state, than it does when in the molecular state. The extended use of ozone would add oxygen in the nascent state, to the list of agents. This question is of much importance when considering the applications of ozone.

We cannot at present have hydrogen in the atomic state without having other agents at the same time. The electric manufacturing of ozone allows of having oxygen in its atomic state and mixed only with the same in molecular state.

Of late there have been chances of a process for the manufacture of hydrogen as H_3, similar to the O_3, according to the possibility opened by J. J. Thomson,[1] who suggested that his X_3 might be H_3. It will, however, take some time yet before the H_3 can compare with our O_3.

1. Engineering, 1913, II, 440.

CHAPTER IV

OCCURRENCE OF OZONE

THE interest in ozone has always been very keen, not only for industrial ozone, but also for the natural.

As we shall learn presently there are tests for ozone which are not specific. When this fact was ascertained all the old investigations based upon the result of such tests became dubious.

There is very much to say for the suggestion of discarding all early determinations, conclusions and information, but that *should not* lead to the tendency to believe that there never was nor ever is ozone in the atmosphere. Although several of the results of these tests may as well be attributed to the presence of agents other than ozone, the action of peroxide of hydrogen, for example, there is no reason to deny the presence of ozone in the air.

Old books, like those of Engler (1873) and Fox, pay considerable attention to the question of ozone in the atmosphere. In former times people seem to have interested themselves very much in the amounts of ozone present in the air; when found mostly, where, in what time of the year, at what hour of the day and such similar points that do not seem of very much importance now.

Undoubtedly there is ozone in the atmosphere, mostly about sunset and sunrise and in the fall and early spring, none at all in cities and probably some at seashores. The amount present surely *never* exceeds one in ten million. There is no reason why there should not be ozone in the air; there are plenty of conditions that permit it, as we shall discuss in the chapters on the manufacture of it. There does not, however, seem to be much cause for so much interest in this particular point; it is said that it is important for hygienists, for meteorologists, and for chemists, but we fail to see any importance at all.

Hygienists cannot profit by the traces that may happen to find their way to a city on very rare occasions, meteorologists

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have to work with large quantities and cannot take much notice of such minute changes as may be found in the ozone contents, and chemists do not care for traces of ozone in the air, since they can have it in the laboratory in large quantities.[1]

The fact that there is so much controversy about the occurrence or non-occurrence of ozone in the air, even at the present time, indicates that interest is still shown on this point.

The many thousands of determinations of ozone-days—Houzeau himself published 4000 of them—are of very little use. Conclusions arrived at by one observer are flatly contradicted by those of another, and small wonder; there are altogether too many circumstances that may or may not have influence on the result.

The different observers, and there are quite a good many of them, tried to establish the influence of: electrical state of the atmosphere, thunder storms, sunlight, force and direction of wind, barometric pressure, temperature, snow, hail and such like, fogs, local situation, forests, lakes, sea, latitude, geographical formation, height above surface, month, time of the day, etc., for different places on earth; well, even several millions of uniform observations would not be enough to eliminate chance happenings out of all that!

As to the actual amount of ozone observed, there is not so much variety; figures range from 0.3 to 1 in a million; even these figures are probably far too high.

As said before, the results of so much work are not reliable on account of the non-observation of the fact that the determination of ozone with starch iodide paper is likely to cause great errors. There are other agents besides ozone that cause the same reaction and the colorimetric test is not to be trusted when it comes to quantitative determination according to shade in color.

Hartley, Chappuis and Schoene examined the ozone spectrum in 1884 and came to the conclusion that the blueness of the sky is due to ozone. Dewar, however, showed that the *conclusion* was wrong;[1] this does not mean that it is not possible that it may still be a fact, it seems even probable and the fact that ozone, either as a liquid or in thick layers as a gas, possesses a dark blue color, rather suggests the possibility that the first-mentioned observers were correct, but there is no evidence at present.

1. Shenstone, in Watt's Dictionary of Chemistry.

CHAPTER V

PROPERTIES OF OZONE

IF we admit that we have in ozone a substance that will easily yield oxygen in atomic state, then its extraordinarily powerful oxidizing property is readily understood and it is useless to state that ozone will turn stannous compounds into stannic, or ferrous into ferric, etc.; it is easy to make a long list in that way, but that is no *specific* property.

In order to show the extraordinary strength of ozone we shall quote some more striking facts.

The organic matter in solution in surface waters is readily oxidized by ozone, to a considerable extent, regular work leading to a reduction of over 40 per cent up to over 80 per cent.

Still more striking is the fact that ozone will oxidize the organic ferric compounds present in waters, leaving ferric hydroxides in suspension.

Ozone will oxidize silver at ordinary temperature (H. Thiele showed in 1906 that a trace of oxide of silver is necessary to start the further oxidation).

Ozone liberates iodine from potassium iodide; it will also oxidize mercury at ordinary temperature; like peroxide of hydrogen it will oxidize lead sulphide to lead sulphate—in fact it does all that hydrogen peroxide will do; after all the only difference being that quantitatively it yields more atoms than peroxide, but all atomic oxygen will act in the same way of course.

What is remarkable about ozone is its strength. Chemists do not realize yet that they can have oxygen in the nascent state in such an easy way and available in any quantity for a very reasonable price.

We must not expect any essential difference between ozone and peroxide of hydrogen, the beauty of both being also that their product of decomposition is oxygen respectively water, a great advantage where purity of the substance to be oxidized is of primary importance.

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The fact that in ozone we have a strong oxidizing agent in the gaseous state is an advantage not to be overlooked; the application of a gas is easy to control and the only reason why oxygen gas is not used, is, that as such, it does not act in most cases; in ozone we are having the gas in its unstable state decomposing to atomic O.

When in the former chapter we said that ozone was a definite substance of its own, O_3, we had in mind the pure gas as it exists theoretically; practically we never have anything else but a very complicated mixture of molecules, atoms, ions, etc., and the best we can do is to consider the complex as a very unstable system consisting principally of O_3 and O_2 when thinking only of ozone made from oxygen gas, which by the way is a great exception, the general rule being to use air as the raw material, so to say.

For the present moment we do better to ignore the presence of nitrogen and all the rest and think only of the oxygen and ozone.

For the sake of convenience we shall use the expression: ozone of such and such a concentration, when we have in view the actual or apparently actual amount of O_3 in the gaseous mixture.

The usual way of expressing the concentration is *not* in percentage, but in so many grams per cubic meter. For those who do not like this rather uncommon but practical denomination, we may add that the weight of 1 cubic meter of air of normal temperature and normal pressure is about 1300 gr.

It may also be added that very often quotations and *repeated* quotations state ozone contents in percentages when grams per cubic meter are meant, and one should be careful about those figures, which in such a case are about twelve times too high!

Whoever has been working with ozone will have experienced its curious effect on rubber and rubber compounds; it is a matter of some seconds only to have rubber tubing eaten through by strong ozone; contrary to the ordinary statement, cork withstands the action very well (unless the ozone be extremely strong), just like wood, and after all cork is but a kind of wood.

It is not far from the truth when we say that taken in a general way, ozone attacks nearly all organic compounds, it being only a matter of time and concentration, but of course there are some that possess a great resistance to being oxidized and when having to handle ozone one has to be careful to use the proper materials.

The presence or absence of water makes a tremendous difference in the action of ozone on the substance in question. Dry ozone is not very active, but we all know that absolute dryness prevents reaction, no matter what substances we consider; moisture is essential to reaction although a trace is sufficient.

In his presidental address before the Royal Society of London in 1909, Armstrong pronounced the doctrine that all chemical change is trimolecular at least, that is, no two pure substances can combine with each other unless a third, acting as electrolyte, be present, and so if we say that absolutely dry ozone does not oxidize, it does not involve contradictions.

Ozone, and by that it is understood that we have it in the ordinary state, not *absolutely* dry, oxidizes most of the metals, but not as readily as one would expect; of the more common, copper, nickel, and tin stand it fairly well; aluminum is easily corroded and so is zinc, also brass and lead.

A coating of shellac protects the metals completely and so do many acid-proof paints of the graphite type or of the asphalt or tar class.

It is of value to know that ozone will change sulphuretted hydrogen into sulphuric acid and probably many of the more complicated hydrocarbon compounds will be oxidized too. This is important when considering the effect of ozone in ventilating problems, as we shall see in the chapter on that subject.

When we know that ozone will change sulphides of the heavier metals like Ni or Co into sulphates and peroxides, it is very probable that the delicate organic volatile sulphur compounds which possess the well-known disagreeable odors, will also be oxidized to odorless complete-oxidation products.

We have said enough now of the action of ozone on different substances and may now learn something about the action of different substances on ozone.

Ozone, considered as a very unstable mixture of O_2 and O_3, is apt to have the ratio $O_3 : O_2$ changed.

Peroxides of lead, or manganese, oxides of copper, silver, or nickel, platinum black, iron oxides, and in general all those substances now known as powerful catalyzers, decompose ozone; that means they shift the point or rather range of equilibrium towards the more stable form—oxygen.

The action of ultraviolet rays is in both directions, that is

to say, strong ozone will be decomposed, and oxygen will be ozonized. This controversy would never have been understood in the days before the development of modern chemistry, that is, physical chemistry. Now we consider the action as one of shifting the point of equilibrium between O_3 and O_2 and so a great many conditions are nothing but equilibrium-shifters.

The action of the brush discharge, the special discharge that causes ozone to be formed from oxygen, also causes ozone to be decomposed, when it is present in an amount above that which corresponds to the circumstances, and that is why we can never make 100 per cent ozone when subjecting oxygen to the electric discharge; the limit seems to be in the neighborhood of 25 per cent according to circumstances of temperature, pressure, etc., taking these about normal. The reaction oxygen→ozone→oxygen follows the law of opposing reactions, that is, the speed of the ozonization is proportional to the amount of oxygen present and the speed of deozonization is proportional to the amount of ozone present. If the discharge be passed an infinite time, a certain definite limiting concentration of ozone will be reached, when the rate of decomposition is equal to the rate of formation of the ozone.

These interesting equilibrium reactions are very often met with, perhaps always, but only the sensitive ones strike us first.

As to the effect of heat on ozone, we have the same thing again, ozone is an endothermic compound, which means that it requires heat (energy) to be formed, but the temperature of formation and that of decomposition lie very closely together, so that it is not possible to make ozone by heat unless very special precaution is taken (see chapter on the manufacture of ozone).

The rate of decomposition of ozone by heat is rapidly increased by raising the temperature; at ordinary temperature it is fairly stable.

Warburg (1902) showed that at 16° C. 1 per cent of ozone per liter of oxygen decomposes in 1.7 minutes, at 100° C. it does so in 0.003 minute, at 1000° C. it is instantaneous; even at a temperature somewhat above 270° C. ozone cannot exist.

A 1 per cent ozone is considered rather strong, the usual amount in practice being about 0.1 per cent or a little over,

and at that figure the rate of auto decomposition is much below the figure given by Warburg for a 1 per cent O_3.

If a mixture of ozone and oxygen be subjected to temperatures below zero, it is possible to obtain a solution of ozone in liquid oxygen, and by boiling off the oxygen, most of it can be removed and liquid ozone remains as a deep blue, very mobile, highly explosive liquid; in this way Ladenburg succeeded in obtaining an 86 per cent ozone (1898).

There is no unanimity about the amount of calories required to convert O_2 into O_3. Berthelot gave the number 29,600, Mulder says it is 32,600, Remsen quotes 36,600 calories per mol. It is a very delicate question to settle. Jahn[1] (1908) gives 34,100, in 1910 corrected to 34,000.

As to the solubility of ozone in water, opinions differ; some say it is not soluble at all, which, however, is very improbable; others say that 100 parts of water dissolve one part of ozone at ordinary temperature and pressure. There are also statements about a greater solubility, that is, ten times that of oxygen, which is 3 vols. in 100 vols.; it will probably be less than oxygen and not more. Ladenburg gave a figure as high as fifteen times that of oxygen at 12° C.

Some ethereal oils such as turpentine, thyme oil, cinnamon oil, etc., are credited with the power of dissolving ozone; it seems doubtful, however. They certainly absorb ozone, but probably do not dissolve it.

There are " ozonators " on the market that contain nothing but cinnamon oil which slowly evaporates. Buyers of those contrivances are supposed to believe that the odor they smell is ozone, and judging from the number of these apparatuses in use, it seems that there are quite a number of people who do believe so.

Oil of turpentine is also said to generate ozone when slowly evaporating; the smell is very pleasant indeed, but that it contains free ozone is extremely doubtful.

In Europe there used to be a trade in ozone water; this, however, containing nitrogen oxide, chlorine, hypochlorous acid, and calcium hypochlorite, is not to be trusted for its ozone contents. By the time that everybody will know the proper smell of ozone, there will be less confusion about it; for the present

1. Zeit. anorg. Chem., 1908, V. 60, p. 357 and 1910, V. 68, p. 250.

moment it does not seem to be difficult to have people believe anything about ozone.

The specific weight of ozone can be determined by the method of speed of diffusion, in so far as Graham's law states that the relative speeds of diffusion of gases are inversely proportional to the square roots of their relative densities. Comparing the speed of diffusion of ozone (of necessity the mixture of this with oxygen) to that of oxygen, we can get an approximate value of the density, and in this way Ladenburg determined the density of his 86 per cent ozone to be 1.3698. This figure is in accordance with the theoretical value of 1.5 (or as 32 to 48) when oxygen is taken as 1. But Mellor calls attention to the fact that we should not attach too much importance to this close resemblance to the true figure, because the above-named 86 per cent is based on the assumption that the molecular weight be 48 as against 32 for oxygen.

The next highly remarkable property of ozone is as a germicide. It is open to discussion whether or not this is the same property as the former, or a specific new one.

Bacteria are destroyed when in contact with ozone, it may be because they are simply oxidized like organic matter, but against this interpretation is the observation that some bacteria are not destroyed, namely some very resisting kinds, the *B. subtilis*, the *B. mesentericus*, the *B. ramosus* and probably some other kinds: fortunately these are absolutely harmless.

Nor does ozone act on some spore-forming germs and that seems to indicate that the highly bactericidal power of ozone is rather due to ozone as such, and not to its oxidizing property.

We have here in mind the use of a low concentration of ozone, say 1 gr. per cubic meter of air (weighing about 1300 gr.); when using stronger ozone it will destroy any kind of microbic life, but we mentioned the action of the weaker gas so as to be able to draw attention to the difference.

We shall refer to this point at length in the chapter on the application of ozone for the purification, respectively, sterilization of drinking water.

The peculiar smell of ozone, pleasant when very, very weak, say one in ten million, has been the object of many remarks; it is unlike anything else.

Do we really smell ozone or is the sensation we get simply the

result of the oxidation of organic matter in our olfactory nerves? The same question turns up if we consider the influence of the inhalation of ozone on our system; does the ozone reach our lungs, or is it all absorbed in the respiratory tract and mucous membranes?

Opinions differ on both points, the author's personal opinion being that here, as in many similar cases, both parties are partly right; ozone of the concentration we are speaking of now, viz., not grams but milligrams per cubic meter, must not be compared to the ordinary agent, unless the concentration be taken into consideration; personally I have been working years and years in my ozone laboratory and consequently have been inhaling ozone almost day after day and sometimes of a pretty strong concentration.

If smelling was not really smelling as commonly understood but a kind of oxidation, a few exposures ought to have been sufficient to destroy the sensibility. It was not; the sense of smelling did not seem to suffer at all, on the contrary, improved as to sensitiveness. As to the action on the lungs, if all the ozone were absorbed before the lungs were reached, it could not possibly have any influence on the blood. The author's personal experience was, that actually the amount of oxyhæmoglobin did improve and the general feeling was very pleasant. In case the amount of ozone inhaled was too much, or rather too strong, mucous membranes were attacked then and a super-sensitiveness was the result, showing there had been overstrain of the membranes. Headache and coughing are the next effect of too much ozone.

It does not seem to call for very complicated physiological experiments to settle the question of the influence of ozone on the human system. Up to now these do not seem to have been carried out by someone familiar with ozone.

In this connection the effect of ozone on the atmosphere as present in dwellings or buildings will be considered.

At the outset we may remark that the effect depends entirely on the amount of moisture present, here again perfectly dry ozone will have no effect on perfectly dry air carrying perfectly dry dust, but those conditions are never fulfilled in actual circumstances. This subject will be treated at length later in the chapter on the application of ozone, but it may be mentioned

here that it would be very improbable indeed that such a strong oxidizing agent as ozone is, even in weak concentration, will have lost that power when having to act on the air we breathe.

It has been said that ozone did not destroy but only masked the bad odors resulting from the perspiration and other volatile organic matter; conclusive experiments conducted by Dr. M. Franklin have shown the fallacy of such a statement. (See chapter on the use of ozone in ventilation, Part III.)

The experiments of Dr. J. C. Olsen are conclusive in favor of the effect of ozone on bacteria floating in the air, carried by particles of dust. The extraordinarily powerful oxidizing property of ozone cannot be reasoned away; it is there and will stay there, no matter how one tries to contradict the fact.

CHAPTER VI

TESTS OF OZONE

WE may distinguish between the qualitative, colorimetric, quasi quantitative, tests for the determination of ozone in the atmosphere and the regular chemical tests.

In the first, use is made of the fact that ozone liberates iodine from potassium iodide, and that this free iodine can be detected by using starch. The well-known blue coloration is an indicator, not of ozone, but of some oxidizing agent, the same reaction occurring with many other substances, such as peroxide of hydrogen, nitrogen oxide, chlorine, etc. Although it may be that the reaction as quoted does not discriminate between several oxidizers, still it is also true that of these, ozone is the more common in the atmosphere, and if there be peroxide of hydrogen in the air, its action is not so very different from that of ozone, so it matters little in most cases whether the atomic O is given off by ozone or by peroxide. There are different ways of ascertaining the difference. Mentzel advocated the use of tetramethyl-base paper; this is not affected by peroxide of hydrogen, but is turned violet by ozone, blue by chlorine, and yellow by nitric oxide. The test paper should be soaked in alcoholic solution of the tetramethyl base.

Engler and Wild stated that when passing a mixture of ozone and peroxide of hydrogen through a concentrated solution of chromic acid, the hydrogen peroxide is alone decomposed, the ozone not being affected.

According to Mellor, the same investigators say that paper steeped in a concentrated aqueous solution of manganous chloride is turned brown by ozone but not by hydrogen peroxide.

Since atmospheric influences, i.e., such as ultraviolet rays in the upper layers of the air, may form peroxide of hydrogen, just as well as ozone, both these substances are liable to be found under favorable circumstances in the air, and determinations

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of one or the other have to be checked so as to be certain about which agent did act on the test paper; that is why many of the old determinations or perhaps all of them should be mistrusted or discarded altogether.

From a practical standpoint it is not of the slightest interest to know how much ozone actually does occur in the atmosphere; there is certainly not more than a trace occasionally.

Of more importance is the question how to make tests for commercial ozonators, as their value depends for a greater part on their efficiency, and this depends on the question how many grams of ozone and of what concentration does the electrical energy turn out in a certain period (generally expressed per kilowatt hour).

The usual way of testing is to have a certain amount of ozonized air pass through a washbottle containing the absorbing agent, and test this for its change.

The reaction of ozone on potassium iodide is usually represented as follows:

$$O_3 + 2KI + H_2O = O_2 + I_2 + 2KOH,$$
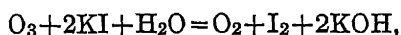
and the amount of ozone can be determined from the amount of iodine, to be measured in the ordinary way with thiosulphate of sodium after acidification of the solution.

It is less accurate, but quicker, when testing the amount of KOH and using congo red as an indicator; this will show its change of color through the brown of the iodine. This method is that practiced by Houseau and endorsed by Andrews.

It must be said here that our own practice was to have the ozone pass through a solution of KI, acidulated with a one-twenty-fourth normal sulphuric acid solution. (This weak acidity does no appreciable harm to accuracy.) The amount of KOH formed combined with the acid and the loss in acid was titrated back with a one-twenty-fourth normal KOH solution from a 100 c.c. burette, so that if 10 liters of the gas were passed through, each cm.^{3} corresponded to grams per cubic meter.

This is easily understood when we reason as follows:

According to the equation 48 gm. of ozone give twice 56 gm. of KOH, so that 24 gm. of ozone give normal KOH, or 1000 c.c. of the one-twenty-fourth normal concentration are equivalent to 1 gm. of ozone.

Suppose, when titrating back, 90 c.c. of the one-twenty-fourth normal potassium hydroxide are used, that means that 10 c.c. out of 100 one-twenty-fourth normal sulphuric acid added to the solution have been neutralized by the KOH formed, which again says that 0.01 gm. of ozone have been passed through (1 c.c. corresponding to 0.001 mgr. of ozone).

Taking 10 liters of ozonized air to pass through the wash-bottle, means that each cubic centimeter of KOH required to neutralize the acid, represents 1 gm. of ozone per cubic meter of air passed through the apparatus.

This method, though less accurate than the usual test, certainly has the advantage of simplicity when a number of determinations in regular every-day work have to be made.

The reactions in acid KI solution are said to be as follows:

$$4O_3 + 10HI = 5I_2 + H_2O_2 + 4H_2O + 3O_2$$
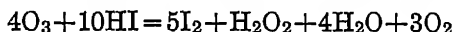
according to Ladenburg,[1] but if one comes to such equations one begins to feel uneasy about them. It is not improbable that the representation will be different when taken into consideration that other possibilities are being left out.

Our regular daily practice allowed of the above mentioned way of testing. Brodie, who published several ozone reactions in the year 1872, says that the action of ozone on iodide of potassium in acid solution depends also on the temperature and the strength of the solution. That same remark may probably also do for the reaction in alkaline solution; the truth, however, about the best method for testing seems unsettled.

Theoretically there is a physical method for the determination of ozone. Since three volumes of oxygen make two volumes of ozone, there is a considerable contraction of volume, but practically we usually work with no more than a few grams of ozone per cubic meter or as said before, about some tenths of a per cent. Now this contraction is quite perceptible when all precautions are taken for constancy of temperature and equality of temperature of the whole mass, but it involves rather clumsy and also delicate instruments to actually carry out such a volume-change test.

If there were any necessity for them many physical methods could be invented, but the chemical method is so simple that it

1. Ber. d. chem. Gesell., 1901, V. 34, p. 1184.

leaves nothing to be desired, when considering ordinary practical requirements; it is of no use to know concentrations in hundredths of a per cent, since the actual composition is one depending on many circumstances such as temperature, moisture, purity of the accompanying air, etc.

It may be mentioned that as a qualitative test the olfactory sense is as good as any reagent.

Graefenberg,[1] who worked a great deal with ozone, says, " I would like to point out that as far as my experience goes, the identification of ozone through its odor is at least as reliable and precise as that by the iodine test, provided of course that the experimenter is used to the particular smell of ozone, and other odors are absent."

We fully agree with him; one can smell ozone long before starch iodide paper turns blue.

In recapitulation of Part I let us say:

Ozone was " discovered " by van Marum in 1785 but was first investigated by Schoenbein, who gave it its name, which means " smell."

It is not uncontested whether or not ozone is O_3 or a mixture of different substances formed out of O_2, but it will be convenient to reverse the question and say O_3 is ozone, leaving O_4 and O_6 for what they are.

The occurrence of ozone in the atmosphere is a positive fact although the quantity is very small. The importance of this occurrence seems questionable.

The properties of strong ozone can be recapitulated in a few lines.

Ozone is an unstable gas, though its rate of decomposition at ordinary temperatures is slow. At 270° its decomposition is fairly sudden. The ratio ozone to oxygen is a function of temperature and time, since it is a question of equilibrium between the two gases. It is an endothermic compound and according to the very latest information requires 34,000 cals. for its formation.

It can be liquefied at temperatures below -119 and as a liquid has a deep indigo color, being very mobile, explosive and magnetic. Ozone seems to be slightly soluble in water; figures relating to this point are very discordant; probably because the ozone gas

1. Zeit. anor. Chem., 1903, V. 36, p. 355.

experimented upon is not 100 per cent ozone but the unstable mixture of O_3 and O_2 containing some few per cent of ozone.

Perhaps also there is some action between water and ozone. Ozone is absorbed to a slight extent by certain ethereal oils; some call this a solution. For the greater part the ozone combines with such oils.

When ozone reverts to oxygen there is increase in volume from 2 to 3 for every part of ozone decomposed.

It is said that ozone exhibits properties of radioactivity. Ozone greatly influences the brush discharge by which it is made, in so far as the conductivity of ozonized oxygen is much less than that of ordinary oxygen under similar circumstances.

As to the so-called chemical properties, these may be summarized as follows: Ozone is a most energetic oxidizing agent at ordinary temperatures and can accomplish reactions never performed by oxygen under similar circumstances. It converts phosphorus, sulphur and arsenic into the corresponding acid-anhydrides; it changes sulphides to sulphates; possibly also nitrogen to N_2O_3 and further to ammonium nitrates and nitrites in the presence of water. Manganese salts are precipitated by ozone as MnO_2.

It goes without saying that ferrous salts will be oxidized to ferric, stannous to stannic, cuprous to cupric, mercurous to mercuric, etc.

Ozone attacks almost all organic compounds; it rapidly corrodes rubber and only albuminoids and saturated hydrocarbons seem to escape from its powerful grip.

It is said to produce phosphorescence with certain organic compounds. Silver forms its peroxide in presence of ozone whenever there is a trace of oxide present; lead is transformed to lead peroxide, in fact all the common metals are oxidized when moisture is present, but the presence of moisture is essential to so many, perhaps all reactions, that it is hardly necessary to mention it.

Iodine is oxidized to I_4O_9, many sulphides are oxidized to sulphates, like the sulphides of Pb, Zn, Cd, Cu, Sb, whereas Ni and Co sulphides form peroxides and sulphuric acid.

In inorganic industrial chemistry there is little opportunity for ozone, its chances are with organic chemistry.

There are some ozonides of interest, and probably within

a short time ozone will be among the important agents for the manufacture of organic compounds. The trouble is that many of the industrial applications are kept a secret, so that reliable information on this subject is hard to get. The most important of all the properties of ozone is its rĕmarkable bactericidal power in water. The bleaching properties of ozone may be considered as the complete oxidation of substances to colorless compounds; it probably does not differ essentially in this way from peroxide of hydrogen. The latter, however, is much more expensive.

As to tests for ozone, for a qualitative test the potassium-iodide-starch paper has the disadvantage of not being specific for ozone but for oxidizing substances; the tetra-base paper, however, is specific for ozone. A keen sense of smell is also of great help; it is the most sensitive of all tests.

For a quantitative test, the original Houzeau test has been discarded on account of giving too high values, and the test almost universally adopted now is that by which iodine is liberated from potassium iodide in *neutral* solution and the amount titrated with sodium thiosulphate after acidification.

Volumetric tests are quite possible but not practicable; the chemical test is quick and sufficiently accurate.

There is abundant literature on all these details, most of which is rather old, but the more recent publications are nearly as contradictory as the older ones, and one has to be very careful when consulting literature and must consider both sides of the question.

We wish to emphasize the fact that in actually manufactured ozone we do not have a pure substance, but a state of unstable equilibrium between ozone and oxygen. Few of the publications on ozone as regards its properties takes the trouble to state what concentration of ozone is meant. The experimenters do not seem to realize the importance of this statement in some cases.

PART II

MANUFACTURE OF OZONE

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CHAPTER VII

MANUFACTURE OF OZONE BY NON-ELECTRICAL METHODS

THERE are several ways of making ozone; a few only have commercial value, but it will be useful to speak briefly of all of them, since they present interesting theoretical questions.

It would be very unscientific to distinguish between chemical, physical, and mechanical methods of producing ozone. If we take things seriously we come to the conclusion that all happenings in the line of material achievement are due to physical causes (taking chemistry as a branch of physics).

The reaction between sulphuric acid and, say, peroxide of barium, yielding some ozone, is no less physical than the electrolysis of water, but the first is liable to be called chemical because the agents used can be bought in a drugstore and bear the name of chemicals.

When an emery wheel flies to pieces and causes thereby some ozone to be generated, we may call that mechanical action, but after due consideration there is nothing new in it, as it is probably a matter of ionization.

We shall subdivide this subject into parts relative to the question of usefulness; that old homocentric standpoint which always remains appealing. We must, however, bear in mind that the question of utility is apt to shift over.

As we have said before there are methods of producing ozone that have none but scientific interest; as examples of these we may mention the fact that when oxygen is being made through the action of sulphuric acid on certain peroxides, barium per-

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oxide, manganese peroxide, lead peroxide, and probably many others, it will contain some ozone. This can readily be understood when we realize that the oxygen, while in its nascent state, has the opportunity to form the triatomic ozone as well as the diatomic oxygen, the question of ratio of one and the other being one of equilibrium, according to the modern views of chemistry, which, by the way, is wholly physical.

The action of sulphuric acid on permanganate of potassium also yields an oxygen containing some ozone; it is probable that any reaction yielding oxygen will also give some ozone, provided the temperature at which it occurs allows of such, ozone being very sensitive to heat.

When oxygen has been made in the ordinary way from chlorate of potassium, the high temperature shifts the ratio oxygen to ozone all in favor of the first, and we cannot expect to get any ozone at all.

When drops of water are allowed to fall into a vessel containing fluorine gas, they are decomposed and the liberated oxygen contains ozone—another proof of the saying, that, no matter how you make oxygen, it will always be partly ozone, unless the temperature forbids.

This condition is not in contradiction of the observation that it is possible to obtain some ozone when passing oxygen over heated oxides, this being possible only when the time of contact is so small that the ozone is not heated up, or in other words, when the ozone is drawn away at great speed. We shall refer to this point again, but may add here, that it is even possible to obtain ozone when directing a minute stream of oxygen at the glowing pencil of a Nernst lamp.

It is disputable whether the generation of ozone through the violent mechanical disturbance of air is due to the heat generated thereby, or to the ionizing effect of same.

When we think only of the fact that heat and heat alone is quite sufficient to convert oxygen into ozone, then we feel inclined to say that the reaction is essentially thermodynamic, and not electric, but in these days of " electricity at the bottom of everything " it is a little hazardous to exclude electricity from a reaction, the more so as it seems to be possible to generate ozone when having Becquerel rays or Lenard rays, or even ultraviolet rays play upon oxygen.

Kruger states that he observed the formation of ozone when using Lenard rays (cathode rays outside of tube). The Curiés reported that Becquerel rays act upon oxygen on account of their contents of gamma rays.[1]

As regards the ultraviolet rays, Regener says that owing to their deozonizing effect they limit the amount of ozone that can be present in oxygen when subjected to the action of the brush discharge; others claim to have made ozone out of liquid oxygen by means of the action of ultraviolet light.

This again is not contradictory; it may very well be that ultraviolet rays decompose ozone and also form it out of oxygen, the action then evidently being one of shifting equilibrium.

The presence of ozone in the upper air is attributed to the action of the ultraviolet rays by Holmes; the same rays account for the presence of peroxide of hydrogen, and there is no reason to deny the existence of ozone in the upper layers of the air, circumstances for its generation being very favorable, or it is better to say that probably all oxygen at temperatures lower than say 270° C. will in course of time contain some ozone as a result of its equilibrium condition, the oxygen in the upper air will certainly be partly ozone. One of the oldest methods of making ozone has been the slow combustion of phosphorus in moist air.

The formation of ozone takes place in such a way that the amount of ozone formed is proportional to the amount of phosphorus oxidized, such that the atomic ratio P oxidized : ozone formed :: 1 : 0.5 says Mellor, but it is not clear what actually takes place. A great number of more or less plausible hypotheses have been suggested, but a crucial experiment has not yet been devised.[2]

If we get accustomed to considering the conversion of oxygen into ozone and ozone into oxygen as a matter of equilibrium, it goes without saying that within a range of conditions, the one will always contain the other, no matter what its origin is; but if we also think of the electrical nature of atomic changes, it is easy to understand, that though it may be quite possible to get ozone by all methods that give oxygen, there will be methods by which the ratio of the two substances will be more favorable to ozone than by other methods.

1. Stewart, Recent Advances in Phys. and Inorg. Chemistry.
2. Mellor, Modern Inorganic Chemistry, p. 579.

CHAPTER VIII

MANUFACTURE OF OZONE BY ELECTRICAL METHODS

By Electrolysis. The percentage of ozone is much higher when making oxygen electrolytically than when making it from oxides, and the regular way of " making " ozone is to have certain special, very special, electric discharges pass through oxygen, either pure or mixed with other gases, say as air.

Electrolytically-made oxygen, may, under very favorable circumstances, contain a considerable amount of ozone, up to as much as 23 per cent having been recorded.

Particularly favorable conditions are a very low temperature and a very high current density, and as an electrolyte, rather strongly acidulated water, preferably sulphuric acid of specific gravity of about 1.1, which means about 15 per cent H_2SO_4.

By electrolyzing 15 per cent H_2SO_4 with a current density of 80 amperes per square centimeter at a voltage of 7.5 volts and cooling to $-14°$ C., it has been possible to raise the concentration to 28 gm. per cubic meter and have a yield of 7.1 gm. per kilowatt hour.[1]

In Fig. 1 we give a curve of the relation between yield of ozone and concentration of sulphuric acid; evidently the point of maximum conductivity does not at all cover that for best output, the first being with an acid of about 1.22 sp.gr., the second at about 1.1 or somewhat less.

FIG. 1.—Yield of Ozone in Relation to Concentration of Acid.

Any other acid gives a worse figure for output, and even the

1. Zeit. Anorg. Chem., Vol. 52, p. 202–229.

addition of any other substance to the pure sulphuric acid causes a decrease in the output.

The potential of ozone against hydrogen is 1.69 volts, and electrolytic decomposition starts at 1.68, so whenever there is electrolysis there is always the chance of obtaining some ozone.

When we realize that up to now very little has been done to improve on the method of ozone production by electrolysis and how promising it looks, it is but fair to suppose that before long somebody will take the matter up.

The probability that the electrolytic method will ever become cheaper than that of discharges is not very great; but one should not lose sight of the fact that cost of production is not solely governed by yield, there being many more items to be considered. Another advantage of the electrolytic method is, that the accompanying gas is oxygen, which can be recovered after its ozone has done the work, and there is also the hydrogen gas to be made use of in some way. Both these gases are marketable at present.

Krenan,[1] experimenting along this line, found that when using potassium hydroxide as electrolyte, the percentage of ozone in the oxygen liberated was far less than when sulphuric acid was used.

It will be difficult to fulfill the two opposing conditions, viz., high current density and low temperature, as only a small part of the electrical energy supplied is used for electrolysis, nearly all of it being wasted as heat, and to carry away heat is not always an easy problem.

Theoretically 1 kilowatt hour should give about 268 gm. of oxygen; it gives no more than about 80 gm., that is about 30 per cent, and thus about 70 per cent of the energy is converted into heat. That heat we are accustomed to call "waste"; not only is it a waste, but it has to be taken away by artificial cooling, which means a further expenditure of energy.

So much for the non-practical methods of making ozone. Their scientific interest lies in the possibility of solving the mystery around ozone and help us know all about its conditions of generation. At present we hardly know any of them, although some scientists nowadays do interest themselves in the question.

Warburg holds the view that the formation of ozone is a photoelectric reaction due to the action of ultraviolet and cathode rays,

1. Zeit. anor. Chem., 1903, p. 403.

but that cannot be, says Kabakjian,[1] since the formation is accompanied by absorption of energy.

It seems probable, he continues, that the dissociation of oxygen is produced by the ions or electrons carrying the discharge, which break up the molecules of oxygen into their atoms, rearrangement of these atoms in groups of three giving rise to ozone.

From a practical standpoint it is important that we should know a little more about ozone because the economy of manufacture is rather low yet, and nobody is able at present to improve much on that. There is ample reason for the hope that in the near future some little detail will be discovered by which the commercial economy will suddenly be a multiple of what it is now.

Probably more attention would have been paid to the above-named process were it not for the fact that the present state of the other method, viz., that of the electric discharge, also promises better results when conducted by modern methods; that is, the technical side of the business is controlled by scientific men, masters of modern physics.

In the ozone field there is no room for the hit-and-miss method of skill without knowledge; there are altogether too many traps, and the effect invariably will be a miss; the failure of many attempts might be a lesson in this line, but here, as in many other cases, somebody else's experience does no good to a tentative beginner, and many a dollar has been lost and will be lost through ignorance covered up by hopeful conceit.

The subject of the electric discharge through gases is one of a special nature and must be treated at length, it being fundamental for the proper design and working of ozonators.

1. Phys. Rev., 1910 (Vol. 31), pp. 117, 122.

CHAPTER IX

MANUFACTURE OF OZONE: ELECTRICAL DISCHARGERS

In order fully to appreciate the value and the role of the solid dielectric placed between the dischargers proper, it is of importance to understand why that system has outlived all the others based upon the non-use of a dielectric.

This chapter will be devoted to the discharge in general, and the next to the brush discharge and its properties in particular, and the conditions and methods of production. It may seem to be too full of particulars or too exhaustive, but it must be considered as a means to prove that the conclusions arrived at are by no means without substantial evidence, derived from actual experience on a large scale during a very long period.

Scientific research, extending over more than fifteen years of study and practical experience, has enabled the author to get acquainted with all the details of failure and success and to come in touch with very interesting instances of theoretical problems and inferences of practical value.

A solid dielectric placed between discharging electrodes completely changes the conditions, and it will be best first of all to treat of the discharges when no solid dielectric is between.

a. Discharges in General. The conduction of electricity through solids, liquids and gases differs according to these states.

It is a fact that it would be possible to devote a whole article to the conduction of non-conductors, paradoxical as that may sound. We shall say a few words about it in the second part, dealing with discharges in connection with a solid dielectric. The conduction of electricity by metallic substances is in its details of little importance for our subject proper; it is sufficient to point out that any potential difference, however small it may be, causes a current to flow, unless we think of extreme cases.

It is thinkable, and even probable, that there will be electrical inertia, in so far, that to start a current—supposed to be a flow of electrons—it will require some potential difference, though infinitesimally small, perhaps partly due to ordinary mechanical inertia of *apparent* mass, perhaps wholly due to electrical properties; it is certain, however, that this minimum potential difference is very small indeed for metals.

In case of a liquid, where we have to consider electrolytic or ionic conduction, the minimum potential difference between electrodes, is of the order of tenths of volts or volts, the value being dependent on the so-called counter electromotive force of polarization.

When there is no question of true electrolytic conduction, the case is rather complicated in character, for instance, when we have to consider a discharge through oil, or pure glycerine, or any other "non-conductor"; but that is beyond our domain now and will not be discussed.

When two electrodes showing potential difference are separated by a gas, then the passage of electricity, generally called discharge in this case, is of a very complicated nature, and that is what we are going to discuss now. Under ordinary circumstances gases are non-conductors, but there are many influences that change them to conductors, as we shall see presently.

If there is no potential difference, there can be no current, but there cannot be any potential difference unless there is a resistance, and it is not a very simple matter to determine what has to be considered as the *prima causa*. Resistance, however familiar to all of us, has to be accepted as a mysterious entity, and thanks to the fact that everybody *imagines* he knows what is understood by it, nobody bothers about it, but surely the philosophical explanation of this common word is by no means an easy problem; let us therefore accept it as we do axioms, and pretend to understand.

Now in ordinary conduction, we have Ohm's law to guide us, but when thinking of discharge in gases there is not such a simple relation between potential difference and current, and the best we can do to get some insight into the matter is to consider volt-ampere graphs.

What happens if we have two electrodes separated by some gas at normal conditions and connected to some source of high-

tension electricity, when the potential difference is being gradually increased?

After having passed a certain minimum—the exact value of which depends on circumstances, but may be in the neighborhood of a hundred volts or so—a discharge occurs, invisible and called dark discharge (not to be confused with the brush discharge, also though wrongly called dark discharge). This dark discharge gradually changes to a visible glow, a bright spot on one of the electrodes; there is very little electricity passing until the next stage, that is, the corona, and then comes the regular brush discharge to which we shall refer in detail later.

Gradually increasing the potential difference between the electrodes, the brush will change to a spark, this again will give rise to the flame and finally the well-known arc will be established.

All of these discharges have their own characteristics. They are not mere gradual changes, but essentially different phenomena.

As the discharge itself changes its own conditions when established, it is impossible to compare one with the other, unless said changes are taken into consideration. Cramp and Hoyle [1] gave two very interesting volt-ampere curves, Figs. 2 and 3; the first named represents the phenomena relating to the primary end of the transformer, the other, those of the secondary, high-tension side.

They hold the view that all discharges pass into one another without any definite break in the curve.

In those curves, the glow sets in at the point A, at B the brush begins and we notice a fairly constant dV/dA, a pretty sudden fall when the flame starts at C and a fairly constant current when once the arc has been established, which of course means a sudden fall in the secondary tension at C.

The graph is very fascinating, but it is questionable whether in all cases the changes are so gradual. There is too much difference in the nature of the discharge, when it is a brush, a spark, or an arc.

Toepler gave parts of curves representing different parts of discharges and these might be compared to the former ones, which amplify Toepler's[2] (1902). See Figs. 4 and 5.

We shall see presently in how far the different nature of the discharges considered do not allow of direct comparison between

1. Engineering, 1908, II, 862.   2. Ann. d. Phys., 1902, p. 477.

one another, for it goes without saying that the flame or the arc discharge with their low resistance and consequently low potential difference, are not comparable to the brush or the spark discharge, which are high-tension, high-resistance discharges.

In order to get more precise ideas regarding these different kinds of discharges it will be best to characterize them as follows:

The invisible dark discharge and the glow are hardly true discharges, for the amount of electricity that actually is leaking is but very small compared to the discharges proper.
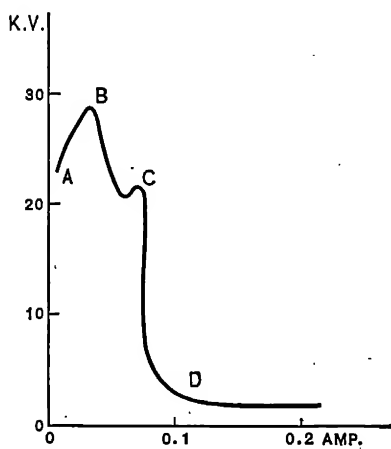
FIG. 2.—Volt-ampere Curve.
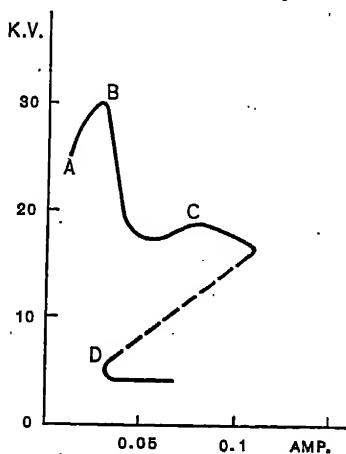
FIG. 3.—Volt-ampere Curve.

The well-known corona effect belongs to the region of the glow, but is a further stage of it, corona losses being a trifle compared with what they would be were they brush discharges; the fact that the critical tension for corona is rather independent of the diameter of the wire, supports the view that it is a kind of glow, this also being independent of curvature of electrode.[1]

The brush discharge is quite another thing—it is a regular discharge of electricity and of a very peculiar character.

In Fig. 6 we see a photo of the true free brush in its best condition; from the electrode it is separated by a small dark space, then comes the straight stem bearing a brush at its end which

1. For corona see the important publications of Peek in Trans. Amer. Inst. Elect. Eng., 1911, p. 1485, 1912, p. 1085; 1913, p. 1332.

extends to quite a distance (the discharge took place in the air, no counter pole being present in the neighborhood). This
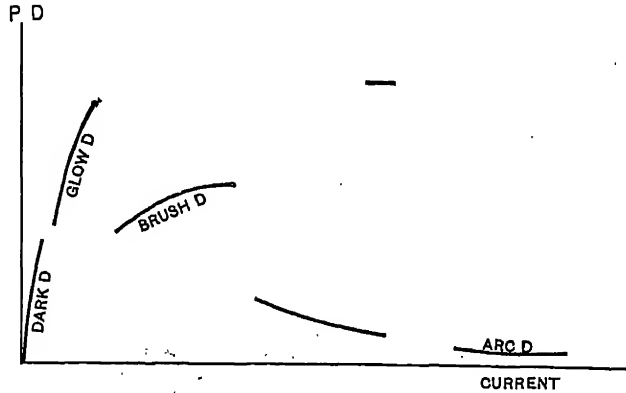
FIG. 4.—Volt-ampere Curves.

brush is of a dark-blue violet color, very steady, accompanied by a peculiar hissing sound and the mysterious electric wind.

That wind, the velocity of which was determined by Holtz[1] in 1880 to be 2.43 meters per second, is explained by Thomson[2]
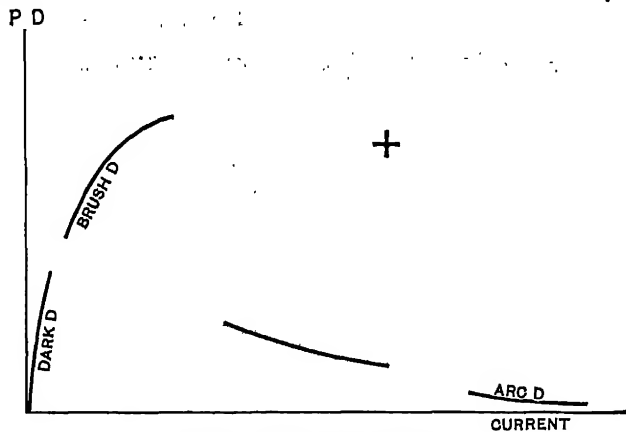
FIG. 5.—Volt-ampere Curves.

to be a current of electrified ions that set the air in the neighborhood in motion.

1. Lehmann, Elektrische Entladungs Erscheinungen, p. 132.
2. J. J. Thomson, Conduction of Electricity through Gases, p. 507.

This forward motion of the air is accompanied by a reaction on the point, tending to drive it backwards, the mechanical force being transferred to the air through which the ions are moving, and causing currents of air known as electrical wind.

Arrhenius[1] found that when positive electricity is escaping, the reaction tending to drive the point backwards is, when the current is kept constant, proportionate to the pressure of the gas, and for different gases at the same pressure, varies as the square root of the molecular weight of the gas.

The reaction for negative electricity is much less, the proportion depending also on the pressure, so, e.g., at 700 mm. and air
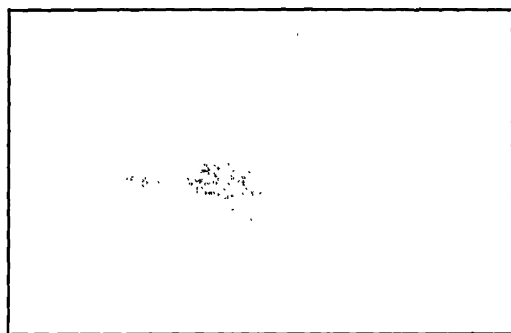
Fig. 6.—Positive Brush.

it is as 1.9 to 1 but at 50 mm. pressure the positive reaction is fifteen times that of the negative. The reaction is due to the repulsion between the electrified point and the ions carrying the discharge.

The ratio of the positive reaction to the negative reaction is greater (and reversed), than the ratio of the velocities of positive and negative ions; but these soon cling to some larger particles.

The accompanying electric wind is not such a simple question as one feels inclined to think. Boon says it is the effect of intense ionization, but that does not correspond with the fact that the brush discharge gives very little ionization. Chattock and Tyndall[2] have shown that the moving of a discharging point

1. J. J. Thomson, Conduction of Electricity through Gases, p. 507.
2. Phil. Mag., 1910 (20), 266.

backwards is not due to the reaction against the air but to the stronger pull at the other end, which suggests that what we have called wind is not wind, but actually blown-out particles.
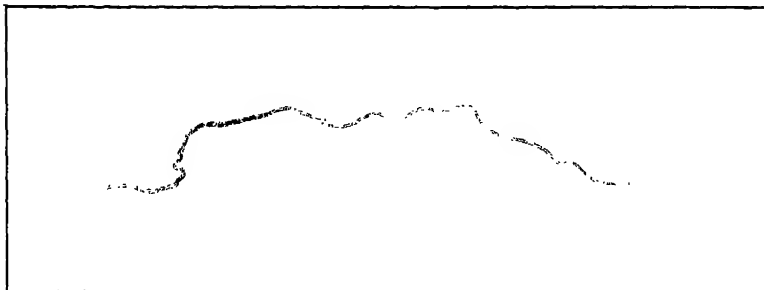
FIG. 7.—Spark Discharge.

It is a common experience that the electric windmill, known as a toy for static machines, will, under certain circumstances, not move backwards as it is expected to do, but *forwards*.

We intend treating the brush more in detail and will merely state that its specific property is to cause oxygen to be converted

FIG. 8.—Ten Consecutive Sparks.

into ozone. Other so-called chemical actions will be considered later.

The next kind of discharge is the spark, characterized by its loud snapping sound, its yellowish color, its zigzag path, or under certain circumstances a straight-line path. Figs. 7 and 8 show some good sparks of 10-in. lengths, Fig. 8 showing ten con-

secutive sparks from the same machine—a powerful 12-plate Wimshurst.

When taken from an induction coil, sparks are apt to be mixed with brush discharges as seen in Fig. 9. This fact accounts for the general mistake in speaking of the generation of ozone by means of electric sparks. The spark will not and cannot generate ozone, but many people who write about the subject do not know or realize the difference between sparks and brushes.

The conditions necessary for a spark are altogether different from those for a brush; a spark pre-supposes the presence of accumulated charge, but not unless there is a certain definite amount of electricity as charge, can there be a spark. Whereas
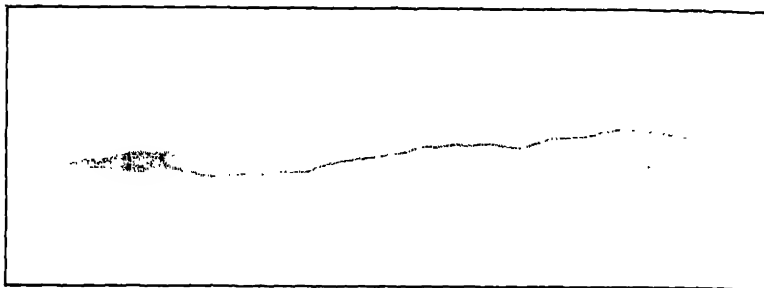
Fig. 9.—Spark and Brush.

the brush represents a gentle flow of electricity, the spark is a brisk rush. In a popular example the one may be compared to a steady flow of water from a small orifice, the other to jets of water from a bucketful. The spark is of a complicated nature; it is an oscillatory discharge and by its existence alters the conditions of its surroundings, thereby also altering its nature.

We have to discriminate between short and long sparks. The study of the former is the more complicated but also has been more investigated, because short sparks have always been at the disposal of scientists whereas long sparks did not enter the field until lately when electrotechnics had come into the foreground.

There are a number of publications about the spark, its relation to potential difference and other circumstances. Baille and Paschen, Warren de la Rue, Liebig, and many others have given figures for spark lengths and corresponding voltages.

It needs no special insight in this matter to presuppose that in a general way the voltage required to start a spark will be dependent on a constant and a varying factor, say $V = a + bL$ when L is the length of the gap.

The factor α, unfixed as yet, represents what J. J. Thomson calls "the extreme difficulty for a charge to get off a metal and on to a gas molecule." Of course this is a varying but not variable factor; the bL factor supposes a linear function of gap length.

To give the reader some idea about the values, be it said that a potential difference of 100-volt per micron seems to be sufficient to tear the electricity carriers from the metal, the other factor greatly depends on the nature and state of the gas in question, such as degree of moisture, kind of gas, pressure, temperature, etc. Taking dry air at normal conditions as an example, we may say that for small sparks but not for *very* small sparks, the curve for voltage distance is like Fig. 10.
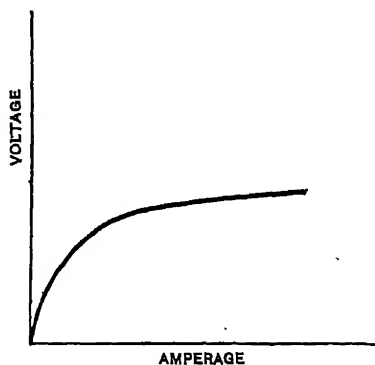
So as to illustrate the extreme difficulty in establishing numerical values for spark length—potential differences, we give in Fig. 11 examples of determination using differently shaped electrode ends. (Warren de la Rue using his cells.)

Fig. 10.—Volt-ampere Curve.

Add to this difficulty that of kind of current supply, if direct or alternating, and in this case, of frequency and waveform, and it will be readily understood that if one says the striking distance to be about 20,000 volts per centimeter it may as well be taken to be 40,000. (The nearest figure seems to be about 30,000 volts for one centimeter.)

For very small distances, say in the order of parts of a millimeter, the influence of all circumstances tells stronger still; quite a new set of phenomena sets in, as in all extreme cases. When considering large distances a new difficulty met with is the fact that for large distances large potential differences are required, but these again give rise to side actions.

At, say above 50,000 or 60,000 volts, electricity starts to flow off freely and it is hardly possible to have true sparks with very high tensions, the brush-discharge mixed with it making a radical change in the circumstances under which the tests are being made.

From all this it may be evident that it is utterly wrong to speak of a striking distance as being so or so many volts per
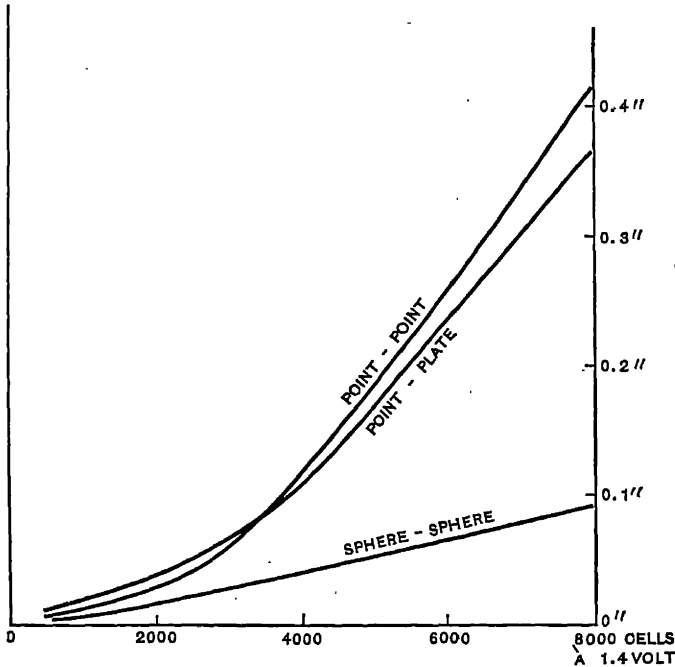
FIG. 11.—Striking Distances for Different Electrode Ends.

centimeter, because there is no linear relation between the two, there is no " per," and the only thing to do is to plot the relation in a graph and give full information about details of conditions.

As we shall see presently, the spark is more complicated than the brush, because we can have the latter without any trouble from the former, but not the reverse.

If we do not consider the spark as given by a static machine but one that may be obtained from any alternating current

source, feeding a pair of condensers, then the spark will be a
straight line, much thicker than the ordinary one, quite steady
in appearance, darker yellow, much shorter, and accompanied
by an almost unbearably loud report. Wireless telegraphy has
made this kind familiar to many. These are short ones, but
they may serve the purpose of giving an idea of what is meant.

This kind of spark is particularly effective in oxidizing nitrogen
to nitric oxide. The author experimented in this lime some fifteen
years ago when the wireless system was not yet in existence.
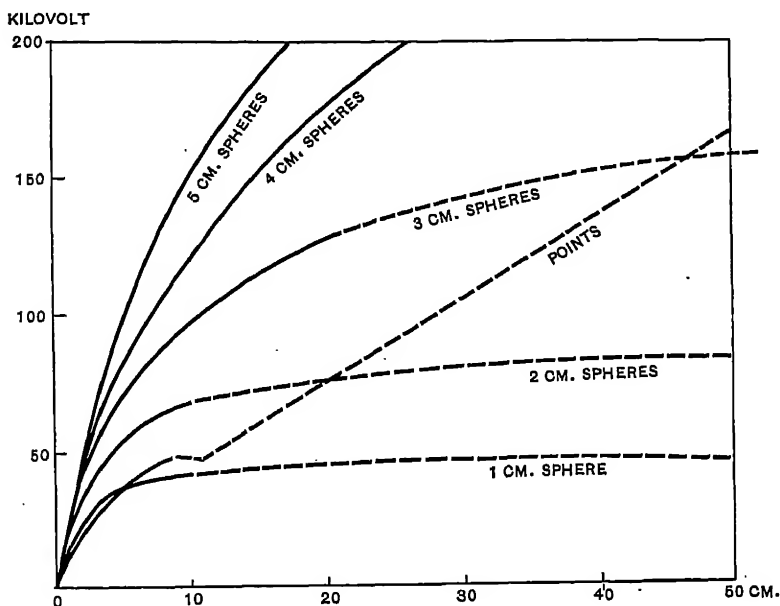
FIG. 12.—Striking Distance-voltage Curves.

This special spark is far more effective than the ordinary
kind. Though it does not differ essentially from it, its powerful
action will probably have to be attributed to its violence. When
we know that a spark is the discharge of an accumulated and
over-saturated charge, it is evident that in case we have to do
with a true condenser discharge, this will be *à plus forte raison*
more powerful (the reader will no doubt understand what is
meant by "true condenser," we know that every trace of
capacity may be considered to create a condenser, but the mean-

ing is obviously a condenser of large capacity). There are a
number of voltage-distance graphs to be had now from different
observers and no longer are we compelled to do with the
determinations made in the laboratories of physicists who, start-
ing with wave-length distances, call centimeters long distances!
Now there are quite a number of determinations available
running up to some hundred thousands of volts and up to
decimeters instead of centimeters of distance.

In Fig. 12[1] we reproduce some graphs that also show the
characteristic difference between the use of a pointed discharger
and spheres of different size. Fig. 13[2] shows in one and the
same series the relation or rather a relation between voltage
and distance, and also the graph for potential difference " per "
centimeter; note the curve and remember the mistake of think-
ing of " per." After all there are but very few functions that are
linear. Of late there has been much very valuable work done in
the matter of voltage versus spark length.

The ratio of the product, critical potential difference times
spark length, to the mean free path of the molecules is apparently
a constant, says J. J. Thomson.[3] That means that for a given
spark length the critical potential difference is proportionate
to the mean free path of the molecules of the gas.

The determinations of minimum potential difference for
different gases, and these relations as given by Thomson, are
also very valuable for understanding the question of brush
discharge. It is to be hoped that some day Thomson will
interest himself in this particular discharge and then we will
be out of all difficulties.

So much for the spark. It may be emphasized that the
spark by its nature does not and cannot cause the formation
of ozone; it does give rise to the formation of nitric and nitrous
compounds, but not to any great extent. The flame as junction
between spark and arc has been given some attention lately
on account of its property of facilitating the combination of
nitrogen and oxygen.

The electric flame has its greatest brilliancy when originating
from a large-power, high-tension transformer, though the potential

1. E. T. Z., 1910, p. 854.
2. Rasch, Electric Arc Phenomena.
3. Conduction of Electricity through Gases, p. 450.

difference to maintain it is only a small part of what is wanted to *start* this particular discharge.

In Fig. 5 we saw how suddenly the secondary tension drops when a flame has been established; it is a *low*-tension phenomenon and a very peculiar one. Its characteristics are a tremendous high temperature on account of the great amount of energy confined in a relatively small space; its color is a pale blue, its form not definite at all but ever changing, it is utterly unsteady
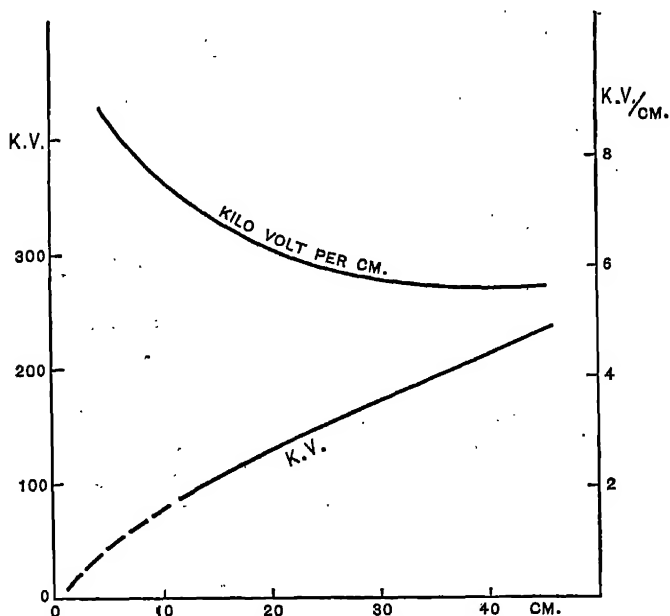
FIG. 13.—Volt-distance and volt-per-centimeter-distance curve.

unless artificially shaped by a magnetic field as shown in Fig. 14 (taken from Prof. Zenneck).[1] There are quite a good many photos taken from flame discharges because the subject is of interest in connection with the resisting power of insulators.

The chief point to consider when speaking of flame discharges is the change in resistance which the air undergoes as a result of the great heat generated. In fact, hot gases are good conductors of electricity; hence the drop in potential

1. Zenneck, Die Verwerthung des Luftstickstoffs.

difference when once the flame is established. The conduction of hot gases which cannot be decomposed is much less than that of gases which do undergo decomposition or dissociation.[1]

Another cause for change in resistance of the gas in question is the discharge itself; this applies equally well to the spark discharge. A gas traversed by an electric discharge is a better conductor than before the passage.
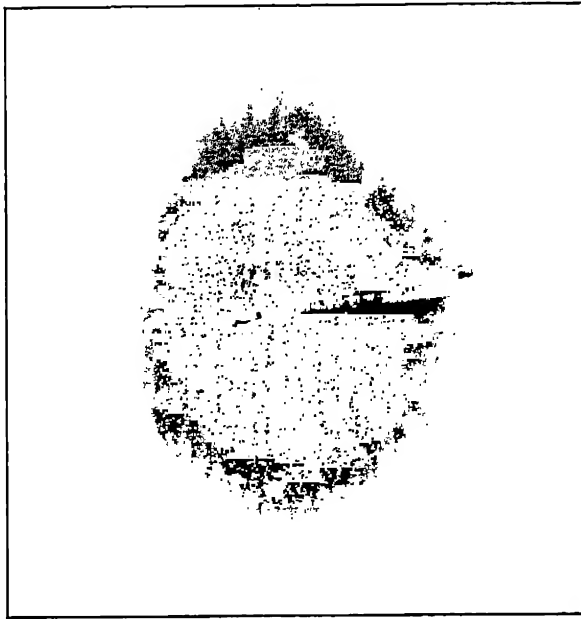
FIG. 14.—Arc in Magnetic Field.

From the flame to the arc is but a step, yet the arc differs in many respects from the former. It is much more steady— as we all know—from the arc lamps; it is also very hot, but less dependent on the gas and more dependent on the nature of the electrodes.

It may be proper here to draw attention to the author's experiments with very small arcs, say something like 2 or 3 mm. in length, and between non-consuming electrodes made of nickel.

1. J. J. Thomson, Conduction of Electricity through Gases, p. 224.

Under certain circumstances it is possible to obtain and maintain an arc between two nickel electrodes or one of nickel and the other of some other metal.

The extreme end of the nickel becomes oxidized to nickel oxide, which seems to have such an extraordinarily great surface-tension when molten that a drop of it remains a drop and gives a brilliant light.

The mystery surrounding this phenomenon is, that when once properly adjusted the discharge goes on without any disturbance at all for any length of time. The electrodes *do not burn* away (which of course would cause increase in distance, and change of voltage required to keep it going) and when observed in a spectroscope no trace is to be detected of any nickel line, the spectrum being the regular one for glowing solids, that is, a continuous one.

Another remarkable fact about this phenomenon is that it is not the positive but the negative electrode that heats up, the former remaining dark unless alternating current is used.

The potential difference between electrodes is about 500 volts when burning; of course it takes a higher tension to start the discharge. It may also be added that the heat is such as to melt platinum like wax, and quartz, or any of the rare earths, are superficially fused.

This little arc is an example of a discharge in equilibrium. It is absolutely steady and presents many details of interest which are out of place here.

The theory of the arc is a matter of much controversy. Mrs. Ayrton was about the first to treat the subject in a thorough way and her book is a standard work although other publications have since appeared.

b. The Brush Discharge in Detail. The brush discharge in particular is a subject of special interest because of its remarkable property of converting oxygen into ozone. The literature on the subject is very scant; hardly ever has an investigator on the subject of discharges found it of enough interest to devote much time to the phenomena involved and yet it is full of mystery and fascinating promise.

Let us in the first place consider one detail, that of polarity. Simple as this may seem, this subject is a matter of dispute. Most people agree on the view that it is the negative brush that

is the more important, while there are but few who agree with the author that it is the positive one.

Fig. 15a and 15b show a positive and a negative "brush," the one to the left being the positive. The other, much smaller and absolutely different from the former in shape, is not entitled to the name of "brush."

It is Warburg.[1] who has been experimenting a great deal on the brush discharge but unfortunately only on a very small scale, using a small static machine as the source of electricity. It is Warburg who is responsible for the "negative" brush
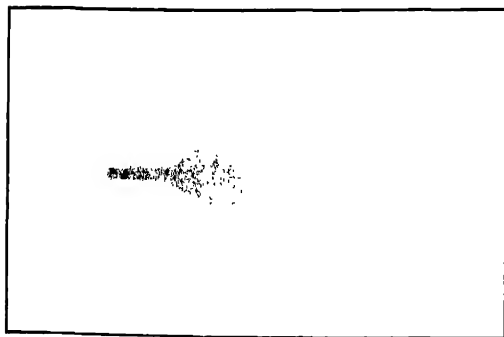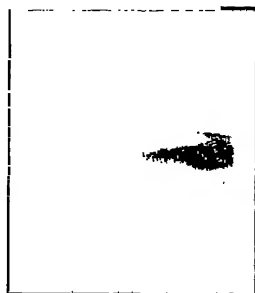
FIG. 15a.   FIG. 15b.
Positive and Negative "Brushes."

stories. He states that the negative brush starts long before the positive, that is, at a much lower potential difference. He also maintains that the negative discharge gives by far the more ozone, although he admits that for smaller concentrations the positive is better. Bischat and Guntz[2] also testified that the negative discharge is the more important for ozone formation. They also experimented with a Wimshurst statical machine, using a thin platinum wire in the axis of a platinum cylinder as ozone apparatus.

Now it is a very common fact with that type of machine that when working it will change its poles and it certainly will do so when one of them is connected to a thin wire.

1. Ann. d. Phys., 1909, Vol. 28, p. 17.
2. Comptes Rendus, Vol. 107, p. 334.

The author's personal experience has been along different lines. A powerful 12-plate, 10-in. Wimshurst (motor driven), several large Ruhmkorff induction coils, up to 16-in. spark, and run with different kinds of interruptors, an ordinary 15,000-volt transformer, a special 50,000-volt transformer each of 2000 watts, and lately a 10,000-volt, 20,000-watt transformer, were
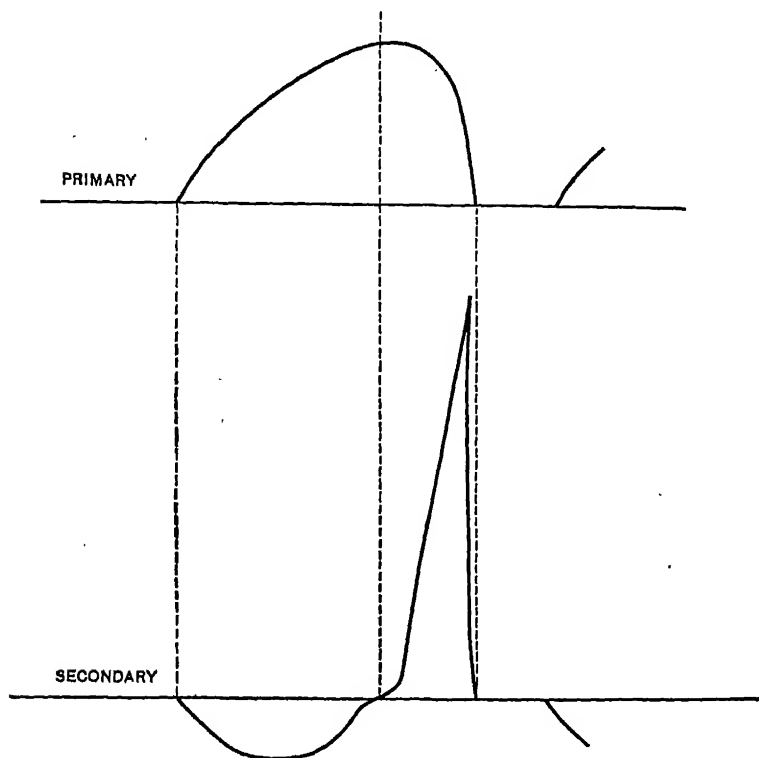
PRIMARY

SECONDARY

FIG. 16.—Primary and Secondary E.M.F. of Induction Coil.

among the sources of current supply. This to point out that the scale on which the work has been carried out is fairly large.

The Ruhmkorff induction coil is a handy instrument for obtaining high-tension direct current. It is well known that though its secondary current is alternating in principle, its secondary waveform is such that we may consider it to be unidirectional. Fig. 16 shows how the great time difference in primary excitation for the make and the break results in a very marked difference in

secondary e.m.f., it being known that the magnitude of this latter depends on the *rate* of change of lines of force, and it is this rate that is so different for both periods.

It may be mentioned here that to learn the polarity of a Ruhmkorff pole one can resort to ordinary polarity paper or even to a strip of wetted litmus paper; a few seconds suffice to turn it red.

When the discharger is not *one* point but a row of say 4000 (steel needles), then if the coil is powerful enough, and the primary current supply adequate, the row will show beautiful brushes all over its length when it is positive, but it will hardly show any
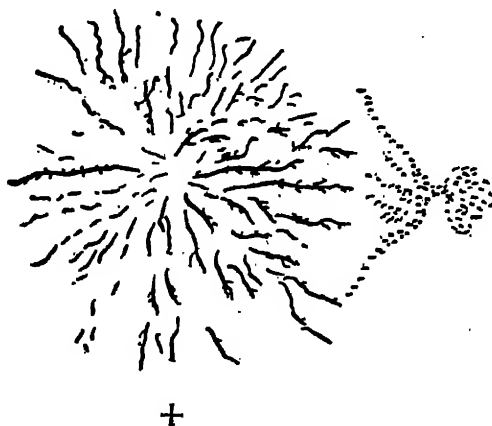
Fig. 17.—Positive and Negative Electroprints.

discharge at all when it is negative. In this latter case all that is to be seen are tiny bright spots scattered all over.

Przibram [1] published a series of experiments on the positive and the negative discharge. His electrographs show the very same prominent differences for the plus and the minus as the photos. See Fig. 17.

Przibram says that the preponderance of the positive over the negative goes *diminuenda* from argon, helium, air, oxygen, hydrogen, nitrogen, carbonic acid, acetylene to chlorine, in which latter case the negative brush is about equal or perhaps some-

1. Ber. Wien. Akad. Wiss., 1899, 2 A. 116/561; 1907, 2 A. 118/1161; 1912, 2 A. 221/2163.

what larger than the positive one; these experiments fully confirm the author's views on this matter.

He says, " that is another instance, and a new support for the view that the positive brush will be so much the more prominent in size and shape over the negative one the more difference there is between the respective movabilities, that is, the greater the quotient $\dfrac{V-}{V+}$ for the gas in question."

Warburg[1] says that points lose their sharpness; Precht[2] says that a point from which positive electricity has been discharged, *sometimes* became hollowed out into a kind of crater as if some of the metal has been torn away. He found that a negatively electrified point did not suffer any change of shape. Other observers, Chaddock and Tyndall,[3] say, that positive points do not age, while negative points do. The author's experience in this line, extending over many years, leads him to say, that there is no aging, no wear, no change whatever in the finest needle points as supplied to him in lots of hundred thousands. Years of daily running of his 2000-watt ozone apparatus, containing some 250,000 points, give evidence of no change, in so far, that from beginning to end there has been no change in the voltage required to obtain the same wattage. Had the points suffered from wear, this would surely have shown in the tension.

So we take the standpoint that the brush discharge is a positive discharge and does *not* cause any wear.

This does not concern the wear on the other pole. Curiously enough there is a comparatively strong wear on the negative pole, in our case a strip of pure hard nickel. After a year's use these counter poles showed streaks as if thin chips had been taken out. One would not expect such a strong effect of the bombardment of gaseous molecules on a metal as hard as nickel.

As to corrosion, the positive points do not corrode at all; the negative strips do corrode, however, and if these are of iron, they soon corrode, even if the air before being ozonized is fairly well dried; this statement, however, should not lead to the conclusion that those who claim the brush to be a negative discharge

1. Am. d. Phys., 1909, Vol. 28, p. 17.
2. Wied. Ann., 1893, p. 50.
3. Phil. Mag., 1910, Vol. 20, p. 290.
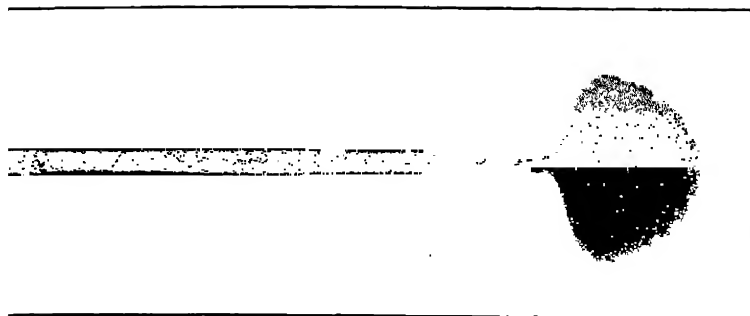
Without Rhoboscope.
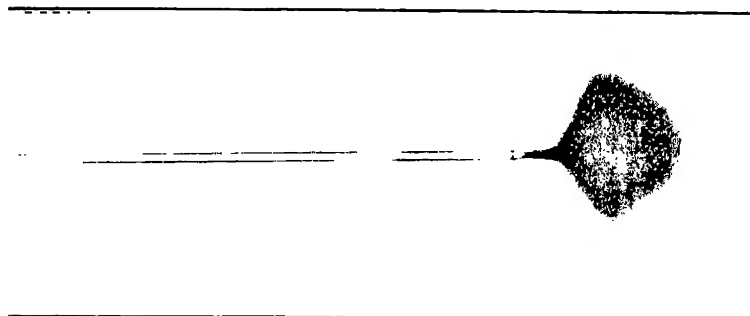
With Rhoboscope Positive.
Fig. 17a.—Brush Discharges,
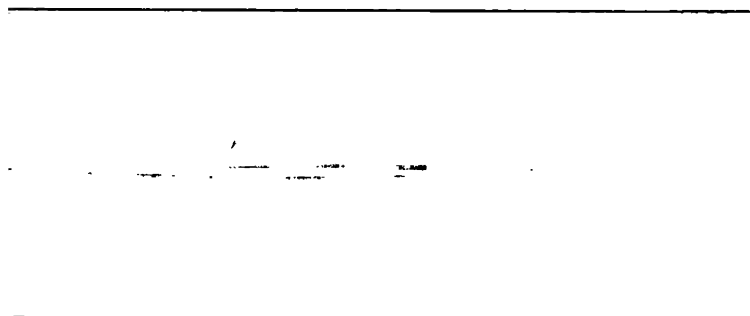
With Rhoboscope Negative.

are right; Thomson[1] has proven that electrolysis in gases is quite another thing from that in liquids; under *certain* conditions oxygen will gather at the negative pole and hydrogen at the positive and it would lead us too far away were we to explain this; suffice it to mention it and to refer to the original for further details. It is an excellent example of the necessity of great care when drawing conclusions.

The beautiful reproductions of discharges from high tension wires given by Peek in his paper before the Institute of Electrical Engineers in 1912 absolutely confirm the view that it is the positive discharge that manifests itself as a brush. The similarity between his photos of brushes and mine is remarkable; in Fig. 17a we reproduce some of them by his kind permission. As we
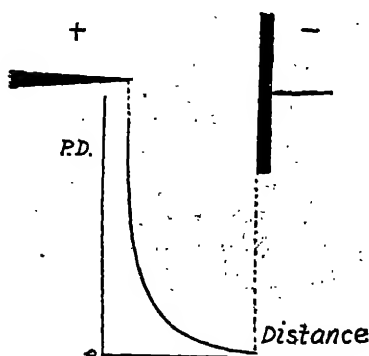
FIG. 18.—Potential Gradient. FIG. 19.—Potential Gradient.
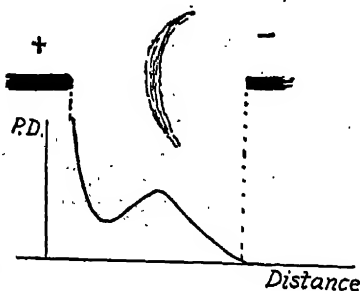
shall see presently for the brush discharge a certain potential gradient is of more importance than potential difference. In Fig. 18 we show the characteristic brush and its potential gradient; Toepler, not using a point and a plate, obtained a somewhat differently shaped line. (See Fig. 19.) In any case we see an abrupt fall at the positive end; later we shall see that it is the stem which is responsible for the generation of ozone. Cramp and Hoyle[2] investigated this point and found, on spectroscopic examination of that part of the brush, almost pure ozone.

There is still another very remarkable property of the brush;

1. Discharge of Electricity through Gases, p. 129.
2. Engineering, 1908, II, p. 862.

it is its desire for space, and if we look at Fig. 20 this can be readily understood.

A very sharp but perfectly smooth edge, like that of a razor-blade, gives a very poor brush discharge, whereas a roughened edge will give good discharges. A saw-toothed edge is still better, and a row of steel needles gives a perfect row of brushes. The stem should be given a support or a base to build itself up. Further on we shall deal with this matter again when speaking of the influence of the electrodes on the discharge itself.

It will be well to call attention to the fact that as the brush discharge is neither silent nor dark, those names often given to it should be dropped; as already said its color and its noise are
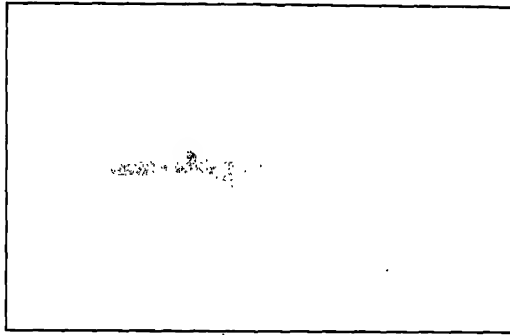
FIG. 20.—True Brush.

characteristic properties. The German name is "Bueschel Entladung;" the French name is "effluve" or "aigrette" according to whether we have the stem only or the full "brush." After thus having dealt with discharges in general, and the brush discharge in particular, we shall proceed to see what are the influences by which discharges in gases are governed.

First of all we have to regard the influence of the gaseous medium itself, viz., its kind, nature, state, pressure, temperature; then we have the electrodes, their form, size, spacing, material, finish. Then there is the current supply, whether direct or alternating, and in this latter case, of what frequency and wave form, the voltage, the amperage, the wattage, also the circuit as a whole as to self-induction and capacity, and resistance. There are also secondary influences, such as radiation, magnetic and elec-

tric fields, and the use of a solid dielectric between the elec-
trodes.

We shall discuss these different circumstances, some of them
at length, others briefly. There has not been time available,
nor the means to investigate all of them personally, and out-
side information is very scant.

c. **Influence of Medium.** 1. KIND OF GAS. Sometimes in
physics we say a gas is a gas, and only when considering the
question more precisely is it evident that it is not immaterial at
all whether we take one gas or the other. So it is when think-
ing of brush discharges, at first it seems as if there were no
difference between them when allowed to pass through different
gases, but on closer observation it comes out, that, as Przibram
pointed out,[1] there is a marked difference whether we take
oxygen or chlorine; J. J. Thomson also drew attention to the
fact that different gases behave differently when subjected to the
influence of electric discharge.

The field is hardly covered yet; personally our time has been
taken up almost entirely by studying the discharges in air because
the object of our investigations was the manufacture of ozone.

We tried some experiments with hydrogen, and with carbonic
acid, but no change in the working of the apparatus could be
detected. It is probable, however, that had we more than super-
ficially looked at it, we would have been able to notice difference,
as it is very improbable that there would be no difference, not
only in numerical values but also in the general appearance of
the discharge.

2. NATURE OF GAS. The question of gases has become much
more complicated since we do not look upon them as being
chemically homogeneous; part of a gas will be atomic, part will be
ionic, and when subjected to the influence of electric discharge,
we may also expect part of it to be electrified. In the chapter
on the constitution of ozone, we mentioned the nine different
substances J. J. Thomson found to be present in oxygen subjected
to electric discharge.[2]

If we admit that a pure and molecular gas be an absolute
non-conductor of electricity, then we also admit that that
condition is hardly ever to be met with, because even a static
charge of an immersed electrode changes this condition. Ioni-

1. Ber. Wien. Akad. Wiss., l. c.   2. Chem. News, 1911, p. 265.

zation is considered to be the direct cause for the passage of current through a gas and its resistance is dependent on the degree of ionization. That explains, says J. J. Thomson,[1] why a layer of gas, twice as thick containing twice as many ions, has only half as much resistance and doubles the current strength for the same potential difference.

Ionization is independent of the kind of metal used as electrode, says Whitehead,[2] but depends chiefly on the curvature of the discharger; he found the value of tension at which ionization sets in to be $32+13.4\sqrt{r}$, wherein r is the radius of curvature; we might as well say it is about 30,000 volts for small radii of electrodes.

If this were so, we could not very well expect a perfect brush discharge at a tension somewhat above 7000 or 8000 volts.

Tamm,[3] experimenting on the influence of pressure on the minimum potential difference required to start a discharge, gives 2140 volts for a negative, and 3760 for a positive point. He considers the current to be carried entirely by ions of one polarity, no matter whether we look upon the positive or upon the negative to be the starter. This is another way of seeing the question of polarity as discussed in a former chapter.

Armstrong objected to the explanation of discharge being ionic in character and considered it to be electrolytic.[4] But, says Arndt,[5] that cannot be, since the discharge does not follow Faraday's law of 96,540 coulombs per mol of substance. In the case of ozone this figure is 500 according to determinations by Warburg.

It is no easy matter to discuss the influence of ionization on the discharge, since this also causes ionization and we have mutual causes side by side. It is curious to note that the brush discharge, powerful as it is, does not seem to be very effective as to ionization; this was quite a surprise to us when looking for it.

3. STATE OF GAS. This refers specially to moisture, also to dust.

Before the time that Steinmetz published his first experiments

1. Engineering, 1908, I, 379.
2. Engineering, 1910, II, p. 840.
3. Ann. d. Phys., 1901, p. 259.
4. Engineering, 1906, II, 312.
5. Arndt, Technische Anwendungen der phys. Chem., p. 112.

on the relation between potential difference and polar distance very many years ago, it was commonly thought or rather expected that a moist gas would be a better conductor than a dry one. He pointed out that it requires a higher tension to jump a gap of moist air than one of dry air. His experiments covered a variety of circumstances and were conducted on a large scale.

The dielectric strength of a moist gas is greater than that of a dry one, but when we only think of the brush discharge it makes very little difference to the general working.

As a matter of fact, we have always been working with dried gas and only occasionally with moist air; the difference, if any, was rather in favor of the moist gas, but it is dangerous to draw conclusions on phenomena not intentionally produced.

For practical reasons one has to use dry gas if one cares about the ozone, and that is an important question without scientific interest.

Particles of dust have very much to do with determinations of minimum potentials. They carry away electric charge by convection, but, as soon as the experiments no longer belong to the domain of the physicist, who works with static machines, induction coils, or batteries, but enter the domain of the industrial laboratory, then dust is not a serious objection, unless accumulated through prolonged use of apparatus.

For the brush discharge dust in itself is a matter of no importance, but it becomes so in course of time and when we have to do with discharges in free air because sparking is provoked, the particles of dust, metallic or non-metallic, serving as vehicles for the current.

Attention may be called to the fact that not until the end of this chapter shall we speak of the changes brought about by the intervention of a solid dielectric between the discharging electrodes; all we consider here is the discharge in free gas.

4. Pressure of Gas. This book would be many times its volume, were we to consider discharges in different vacua. Quite a mass of literature is to be had on the subject of discharges in vacua, chiefly because those bring the physicist nearer to molecules.

This book treats only of discharges in plenum. It may be mentioned that the brush discharge is rather sensitive to change of pressure in so far as pressures both higher and lower than atmospheric hinder its development. A diminution of pressure

changes the brush at once, sparks are liable to occur, stem and aigrette are liable to be less accentuated and the discharge more closely resembles streaks instead of brushes.

When experiencing the change in this direction one feels inclined to expect improvement at adverse conditions, viz.: increase in pressure, but that is not the case; at higher pressures (we tried up to two and a half atmospheres) the discharge takes more and more voltage for the same wattage, the brush again changes its appearance, becoming more and more faint, sparks are liable to come because the tension has to be raised on account of increased resistance.

Many years later it became more generally known that high pressures are unfavorable for discharge. Watson built his static voltmeter on the principle that at high pressures air is a better insulator than at ordinary pressures.[1] Different figures have been given for the dielectric strength of compressed air, and to give an idea as to what extent it is affected, we may say that the voltage required to send a spark from one sphere to another is about 20,000 plus 25 times the pressure in atmospheres when we have a 1 c.m. air-gap.

As said before, one should never lose sight of the fact that very few functions are linear. The use of the little word " per " should be restricted to some very special cases. And another remark may be made: it is this—that it is not only quite superfluous, but even harmful to give very approximate figures in decimals. The discharge of electricity in gases is of such a complicated and little understood nature, that it is better not to assume the air of accuracy.

It is interesting to know that the conductivity of liquefied gases is very low, that of liquid sulphur dioxide being of the order of that for pure water (1×10^{-6}). Is this on account of the low temperature, or notwithstanding?

The reply to this question is not so easy as it seems.

5. TEMPERATURE OF GAS. A hot gas is a perfect conductor. As low a potential difference as a millivolt may cause a current to flow through red-hot air, says Blondlot,[2] and J. J. Thomson found that different gases conduct with different degrees of facility, it being a matter of dissociation.

1. El. World, 1909, p. 932.
2. Comptes Rendus, 1887, V. 39, p. 355.

Now there are two kinds of dissociation to be regarded, viz.: that whereby the gas in question is split up into atoms, as is the case with such gases as iodine, and that where the gas is split up into simpler molecules, say steam into molecules of hydrogen and of oxygen. In this latter case the conduction is very much less than in the former, says Thomson,[1] and he attributes the effect of heat to decomposition. If there is no atomic decomposition the discharge has the character of a convection current.

It is curious to learn from him that vapors of sodium, potassium, cadmium, bismuth, lead, aluminum, magnesium, zinc, and silver conduct well, whereas those of tin, thallium, and mercury hardly conduct at all. The brilliancy of the mercury arc lamp would by itself not suggest the non-conductivity of mercury vapor, but in that lamp there are other agents at work as well.

So speaking in a general way we may say that increase in temperature greatly decreases the resistance of gases, but the temperature at which this change takes place is specific for different gases.

In our case of discharge no change could·be observed whether the temperature was fairly low—say minus 25° C.—or fairly high, say plus 50° C. We had no occasion to try further on the scale. It is probable that the brush will cease to be a brush when the temperature is above 200° C.

The experiment is rather difficult to perform, as at high temperatures all substances known as insulators become conductors, and all good conductors increase in resistance; glass is a good conductor (electrolytic though) at about 600° C.,[2] so no wonder that air conducts at that temperature.

In order to have the best effect of the non-conduction, the temperature of the gas should be low.

d. Influence of Electrodes. 1. SHAPE. Now comes the cardinal point for the brush discharge, the form of the electrode. A perfectly smooth and spherical or plane surface does not realize the first condition for a brush, namely, a point or sharp edge, the brush being a gentle flow of electricity.

Just as it is rather difficult to obtain sparks between pointed electrodes—it is the brush that prevents this—the flow of elec-

1. Discharge of Electricity through Gases, p. 98.
2. v. Warburg showed that even at 200° or 300° there is conduction.

tricity prevents the charge from becoming accumulated, and thus prevents or hinders the spark.

The way to obtain brushes is to have sharp-edged or pointed dischargers. Just what happens when a point discharges electricity is not quite settled yet; Chattock[1] says it is a question of how far the pull at a discharging point is due to the field at its surface, and how far it is due to purely mechanical forces brought about by the discharge. In case of a positive point, however, the only force of any importance is the former.

Now in order to have a strong field at the point, its curvature should be as large as possible, that is, its radius as small as possible. We shall see presently what shape the other pole should have.

If we think in a general way of shape of electrode ends, we think of points, edges, spheres, planes and wires.

We can have brushes from spheres but it is not so easy to maintain them, unless there is no other metallic opposite pole in the vicinity; spheres are the right electrodes for sparks and so are planes, not wires (of course we mean thin wires). A gentle, steady flow of electricity cannot be expected from a sphere or a plane; a thin wire will do but not always, as we shall see.

Before proceeding we have to point out that there is still another question to be considered, viz., that of polarity. We know already that unless the point or edge be the positive, there will not be a discharge; but then comes the question, what shape should the other electrode be? There are a great many combinations possible between these five different shapes and two polarities, but most of them turn out to be the same as to effect.

A few of the more important may be mentioned. Take two flat electrodes; the discharge will take place at one of the edges as it is here that the circumstances differ from the rest. Here it is that the electric charge is largest.

No discharge whatever can start from the centers; if the edges are well rounded off, no brush will be obtainable; a spark may occur however.

Now take two spheres; there can be no brush again, but a spark will easily pass.

1. Phil. Mag., 1910, 266.

If both spheres are of the same size, the equipotential surfaces are spherical shells, concentric with their spheres, and that is no suitable condition for a brush discharge.

Two parallel wires if smooth all over, do not allow of brush discharge. Here the equipotential surfaces are coaxial cylinders or so. Two crossing wires may give rise to a brush at the point of intersection, but a wire is not a very suitable form, and fortunately too, for that is the reason that the corona loss from wires does not amount to much.

Two points or two edges do not give good brushes, though something of it may, under very favorable circumstances, be seen, and if we look at Fig. 21 it is all very plain, as the origin and the
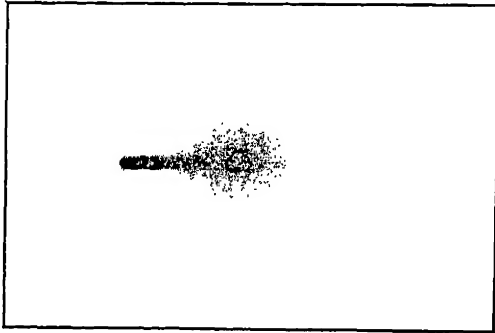
Fig. 21.—True Brush.

end of the discharge are quite unlike in form and hence they should not be expected to fit themselves to like electrodes.

The same figure at once suggest the use of a point or an edge and opposite a plate or a strip. This is the right way.

The rapid fall in the potential gradient indicates the necessity of a special arrangement. We meet the conditions best when we take a positive point discharging against a negative plate or a row of points against a strip.

Of course a positive sphere of small size will also discharge as a brush against a negative plate and so will a positive wire of small diameter; no arrangement, however, will do when the sharp dischargers are made the negative pole.

In Figs. 22, 23, we see some examples, the spark being represented by a zigzag line, the brush by a brush line, a thin

blue spark, something midway between an ordinary spark and a
brush, by a tiny straight line and a negative discharge by a
point. This figure will show the different discharges at a glance.
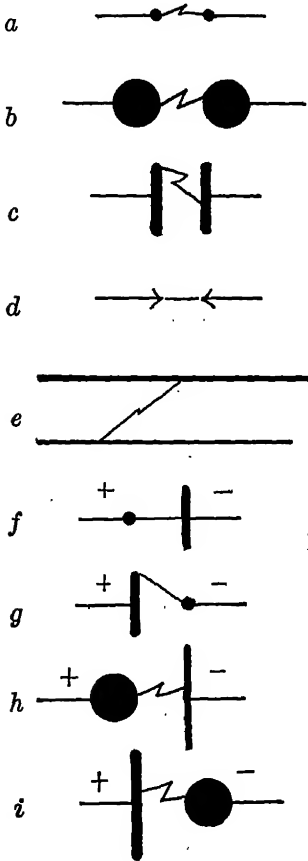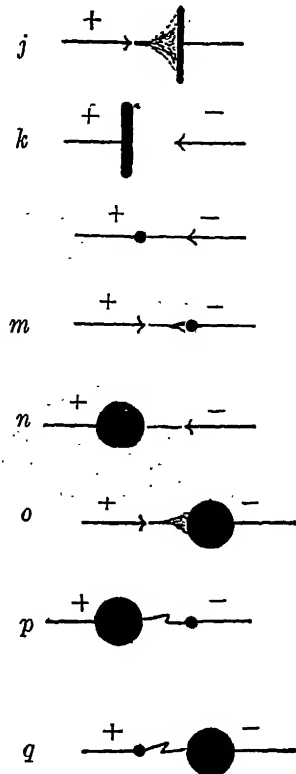
FIG. 22.   FIG. 23.

Discharges from various electrode ends.

The practical side of the question is very simple indeed. If
one wants good pure sparks, use large spheres or one sphere for
the positive and a plate for the negative; but if one wants good
brush discharges take one point or a row of them for the positive
and a plate or a strip for the negative pole.

All this of course refers to the discharge from a direct-current supply, if—and this is generally the case—the supply is high-tension alternating current, then just the same thing holds good, the only difference being that owing to the rapidity of change of polarity, we do not notice that there are moments of no discharge, viz., the moments that the points are negative.

How to make up for the loss of time (not of energy of course) is a simple matter. Connect a set of sharp electrodes to one of the main wires and another set to the other wire; then the negative period of the one will be compensated by the other, being positive at that moment. Fig. 24 exemplifies this idea by having electrodes made in such a way that they are sharp at one side and flat at the back, so that one electrode serves the purpose
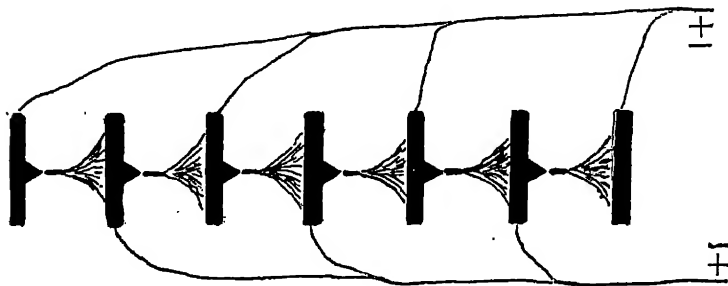
FIG. 24.—Connection of Dischargers.

of positive transmitter and negative receiver, to express it in a popular way.

2. SIZE. The size of the dischargers is also of much importance when considering sparks, because the size of the spark depends on the amount of charge accumulated before discharge takes place, but it is of no importance when having in mind the brush discharges. Still something has to be said concerning this point; when we look again at Fig. 21 we see a certain spreading out at the base, that suggests that it is not altogether immaterial what width we give this negative pole. Practice has shown that it is right when we take this width about the same as the polar distance or a little over that value.

By way of example of the influence of the width of the counter pole we will mention that a certain discharger gave 100 watts discharge when its counterpole was only 6 mm. wide, and

150 when said width was increased to 16 mm.; there was no further increase after this.

The size of the positive discharger does not matter at all as long as the points are not extremely short; we then have some trouble from the electric field at its back.

If we take dented strips in the style of fine saws the height of the dents should be about the same as their spacing apart.

In our first 2000-watt ozonator we used rows of steel needles for one discharger and nickel strips for the other; as said before, the number of needles amounted to as many as 250,000 and when having to build an apparatus for 20,000 watts the construction had to be altered on account of high cost of manufacture.

We then had recourse to dented nickel strips of one-half millimeter thickness and provided with little teeth of one-half millimeter height and spaced so that thirty-six of them went to the inch; it will be of interest to know that the 20-kilowatt apparatus delivered its energy through over one million of teeth all in the form of brush discharge. The polar distance was 13 mm., the width of the negative strips 16 mm., the tension being a little over 10,000 volts.

In Fig. 24a we see some different arrangements of electrodes. As to wattage and output in ozone, it does not make any difference at all how we arrange dischargers, provided we take all other conditions into consideration. A too crowded arrangement results in more energy per surface of apparatus, and thus causes more heat, or rather provides for less radiating surface. Of course, that will have influence on the output, but where we say it is immaterial how dischargers are arranged, it is understood that conditions remain alike or are accounted for.

3. SPACING. The spacing of the electrodes is a very interesting question. As said before, a razor-blade edge will not give good brushes, there being no discontinuity and hence no opportunity for the stem to build itself up, but if we make a row of points, there is no trouble about it; there is no limit to the length as long as the supply of current is large enough to feed all the points, but we cannot have several rows spaced at liberty; there must be ample distance between them. Suppose we take one discharging strip, a (Fig. 25) provided with a row of points, all goes right when circumstances permit; viz., if we have the proper polar distance and the proper tension, etc.

If we then place another one, *b*, next to it (see Fig. 25), if the spacing is not adequate, the brushes will not be fully developed; if, however, the dischargers *a* and *b* are at the right distance, it is all right.

Suppose a third discharging strip, *c*, is added to these two; then if they are too close together, the one that is in the middle
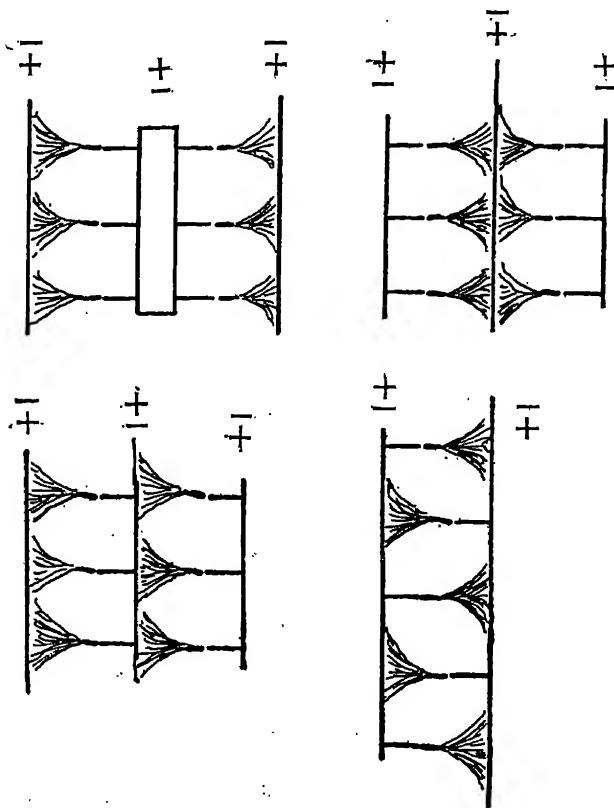
FIG. 24*a*.—Different Arrangements of Dischargers.

does not discharge at all, and not until the mutual distance is the proper one, will there be discharge from all three, *a*, *b*, *c*.

This interesting case of mutual hindrance of discharges can be easily watched during the working, when said discharging strips are mounted in such a way that they can easily be moved sideways.

One can go on in this way, adding a fourth, a fifth, etc. The result will invariably be that none but those at the end—the first and the last—will discharge, all the rest will be extinguished, until after moving them apart the right spacing is obtained.

This at once explains why one cannot have brush discharges from a plane surface, and it also points out the essential difference between discharges without and with a dielectric between electrodes; in this latter case there is no trouble of this kind.

This peculiar property is rather unfavorable for the design of practical ozonators, because of the larger size of apparatus required; on the other hand, it provides for the necessary cooling surface without special care.

It is an interesting case of what is called the influence of electrical shadow. It should also be remembered that as at greater polar distance the spreading out at the base is larger, so the spacing should be in accordance with the polar distance; as a rough measure one may take about the same value for both.

We shall see later that the question of electrical shadow, or influence of electric field, is one that is rather troublesome in actual practice.

Another point noteworthy of remark is, that it is not such

FIG. 25.—Spacing of Dischargers.

a very simple matter to have the discharge in proportion to the length of the dischargers *in toto*, and that is a very sound proof of the value of the ozonator as such, viz.: is the wattage taken up by the apparatus in proportion to the number of dischar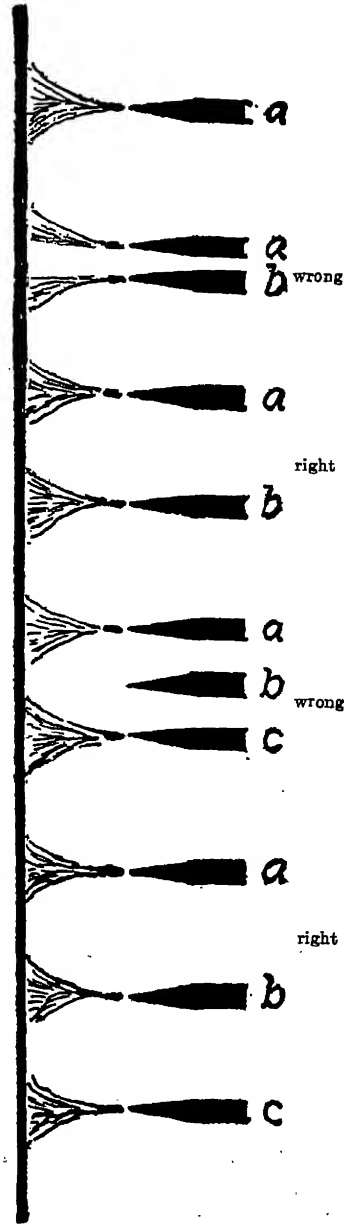ging units, no matter what these are; it is a most puzzling difficulty for everyone starting in this line of work how to establish proportion between electrical energy and discharging units.

Add to this the difficulties of phase shifting, as a result of the large amount of capacity brought into the circuit, and one need not wonder about the many failures of large ozonators that worked so well on the initial small experimental scale.

4. MATERIAL. The material from which the dischargers proper are made is of no importance as regards electrical effect; for purely practical—including economic—reasons, we have to make our choice from those metals that will stand the action of ozone and are of sufficient rigidity to allow of good workmanship and thin dimensions. As said before, steel and nickel are satisfactorily used; it may be that among the modern alloys there will be some that suit the purpose as well or perhaps better. One of them, the well-known nichrome, seems to fulfil all the requirements of a suitable material. It can be had in thin dimensions, is practically non-corrodible, hard, and stiff and not too costly.

5. FINISH. The finish of the electrodes is of importance, since any roughness goes in the direction of points. It is advisable not to use polished surfaces as it is of advantage to create artificial discontinuity of surface, but sharp edges and corners should be avoided at those places that must not discharge.

e. **Influence of Current.** 1. VOLTAGE. There is first the question of tension. One look at the curve for potential gradient is enough to abolish all thought of a tension " per " millimeter of air-gap; we can only say that the character of the brush discharge does not allow of a free air-gap smaller than about 7 mm.; even 10 mm. is rather small and our regular work has been with a 13-mm. air space between electrodes.

For secondary reasons we had to look out for the smallest possible polar distance (this giving the highest yield of ozone). That polar distance of 13 mm. settles the tension; within narrow limits it has to be about 10,000 volts. When the polar distance

is taken too small there is trouble from sparks instead of brushes, and the same is the case when the tension is raised too much above its normal value.

There is no difficulty whatever in using higher voltage provided one regulates the polar distance accordingly, but there is no advantage in doing so; on the contrary, there are many disadvantages.

Schneller was the first to deviate from the regular practice (in 1894); he used no dielectric between the dischargers (see further in the chapter on ozonators) and employed tensions as high as 50,000 or 60,000 volts between transformer terminals. He intersected a high resistance, measuring some 20,000,000 ohms in the circuit and used a 25- or 30-mm. polar distance between electrodes.

That last figure for polar distance gives us the value of the potential difference to be about 16,000 volts. We must remind the reader that discharges through gases do not at all follow Ohm's law, or it is perhaps better to express it this way: The resistance of a gaseous path is not a simple function of its length and width; volt-ampere curves are by no means straight lines; a slight increase in voltage causes a big increase in amperage. Fig. 10 is a typical volt-ampere curve.

A remarkable mistake has been made by Leon Gérard, who in his enthusiasm for high tension (probably due to the fact that he *has* to use it on account of having two dielectrics and a large air space between electrodes) said that it is of great advantage to use high tension, "since for a given wattage a great amperage means a great amount of heat and heat is detrimental to ozone production."

Now of course heat is a transformation form of the supplied electrical energy, but the amount or the temperature does not depend on the magnitude of either current strength or tension, but on their product. So many watts correspond to so many calories no matter how the product volt×ampere is made up.

A very high tension appeals to many experimenters and so does a large polar distance. The discharge certainly looks very fine when playing between some centimeters distance instead of some millimeters; the beauty culminates in the Tesla high-frequency discharges, but it is not the beauty of the sight that we are after, but the most economical conversion of oxygen into

ozone, and that is not a matter of taste, but one of figures and hence easily settled.

It is Chassi who said that the yield of ozone corresponded to voltage, and he even went so far as to give a graph, see Fig. 26a, but that must be a mistake. It is not so easy in the case of discharges through gases to vary the tension without at the same time also varying the energy.

By way of example we may say that when for a very small apparatus the polar distance was taken 13 mm. the wattage was 130 and the yield 10 gm. per kilowatt hour. On increasing the polar distance to 16 mm. the wattage could be raised to 170 but the output fell down to 7, and when further increasing the polar distance to 22 mm. the wattage was 190 and the yield only 6.
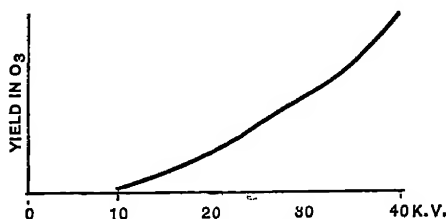
FIG. 26a.—Yield-voltage Curve.

In Fig. 26b we give three graphs relating to the influence of polar distance on voltage, wattage and yield of ozone, respectively.

We see how the voltage is represented by a nearly straight line. The wattage of course is a curve, since the amperage is a complicated function of the voltage, as shown in different graphs.

The yield curve is nearly straight too; it shows that it is a big mistake to believe in large polar distances; surely the wattage is increased but that is not what we are after, it is the yield, and that is decreased on increase of polar distance, hence the great advantage of the use of a solid dielectric between electrodes; it allows of much smaller polar distance.

This view is confirmed by the fact that the famous Tesla discharges hardly give any ozone at all when compared to that of other discharges.

In conclusion, as to voltage it may be said that this plays no rôle other than that of a force and hence it should be as high

as is consistent with the prevailing conditions of the discharging apparatus as a whole; not on account of a higher voltage but on account of a higher wattage. It is most economic to run an ozonator at its best, but there are other reasons to limit this desideratum, viz., in case we have no dielectric it is the danger from sparks; in case there is a solid dielectric it is the danger from cracking or perforating, as we shall see later.

When we realize that the voltage cannot be under and not be over a certain value, it is easy to understand that the wattage
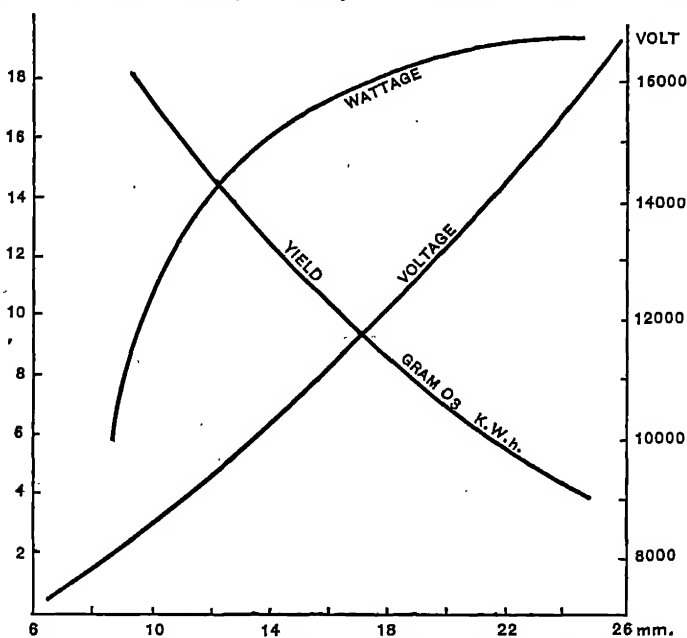
FIG. 26b.—Relation between Wattage, Voltage, Yield, and Polar Distances.

depends greatly on the amperage and this of course depends on the size of the apparatus.

Ozone production is a question of transformation of electrical energy into chemical, and thus bears on wattage, and since we cannot greatly change the voltage for a given apparatus the quantity of ozone depends on amperage. Gray was about the first to recognize this simple fact in 1905,[1] and in 1910 Kabakjian[2]

1. E. T. Z., 1905, p. 518.
2. Phys. Rev., 1910 (Vol. 31), pp. 117–122.

confirmed the view that ozone has no special relation to voltage, and we may safely take it for granted that they are right.

As the output in ozone per kilowatt hour rapidly increases with increase of wattage per available space, it is a common mistake of all those that start on this line to overrun the apparatus, thereby obtaining good figures for yield but at the risk of frequent breakdowns. There should be proper harmony between the energy supplied to an apparatus and its size.

2. KIND. It is a curious fact that it has not been settled yet whether a direct or an alternating current gives better results as to discharge and ozone production. There are not so very many people who have high-tension direct current at their disposal, when we take leave of such laboratory instruments as static machines, induction coils or high tension rectifiers.

It seems very probable that the high-tension direct current will be found very well suited for the purpose, but at present we must be satisfied with what is known about the high-tension alternating current discharge.

3. FREQUENCY. We then have to consider the influence of the frequency. A higher frequency than the customary 50 or 100 is favorable to the brush discharge and to the ozone production. We tried up to as much as 500 and found a decided advantage.

Milton Franklin goes as far as saying that the yield of ozone is a linear function of the periodicity of the current, but the practical limit is given by the fact that in order to keep pace with the increase in energy supplied in a given space, one should also increase the amount of air passed through the air space. This, however, is one of rather limited width and the resistance offered to the passing air soon puts a stop to further increase in quantity, and if one does not increase the amount of air in ratio to the energy increase, the ozone will be the more concentrated and that again decreases the yield.

We do not know of any graphs showing the proper relation between periodicity of current and yield per kilowatt hour, but judging from the fact that most of the modern ozone plants are using a frequency of 500, it is probable that this will be about the best figure.

The gain in economy does not hold when further increasing the frequency, and when we come into the domain of the so-

called high-frequency discharges of Tesla we are very far from obtaining the best results.

It is true that the brush discharge goes very easily then, there being very little danger from sparking, and the polar distance of electrodes can now be made either very much larger or smaller than generally used, but as to ozone formation, this seems to suffer greatly from this change; the output per unit of energy is extremely low.

We have to distinguish here between the effect on the discharge as such and on its application for ozone making. The first is influenced very favorably, the second very unfavorably, up to detrimental.
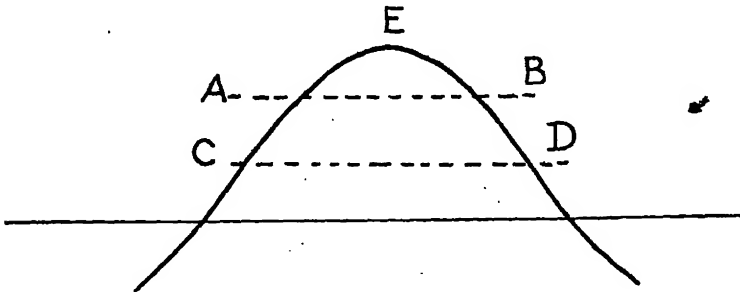
FIG. 27.—Voltage Curve.

4. WAVE FORM. Another point of some importance is the question of wave form.

When we consider Fig. 27 and realize that the possibility of brush discharge without spark is given by the fact that when the polar distance of dischargers is made according to the striking distance for sparks, viz., maximum voltage, there can be brush discharge at a much lower voltage, say between the lines *ab* and *cd*. Under this limit *cd* there is no discharge at all.

Now when using sharp-pointed dischargers, the wave current never reaches its ordinary maximum; long before that moment the electricity has flown off and by so doing prevents its own accumulation. The actual wave will be like *ADC* instead of the original *ABC*; see Fig. 28.

That is in a popular way the explanation why brush discharge can be had from points, or, what amounts to the same thing, why sparks cannot be had from points. A very peaked

wave form would cause a greater distance between regular working
tension and ordinary maximum tension and thus facilitate the
brush discharge. On the other hand, a flattened curve would
give more available energy in the domain of working and would
give a better output of ozone.

In actual practice there is not so much difference in wave
form of current machinery to be of any importance, moreover
we generally have to put up with what we get.

f. Influence of the Circuit. This is a very difficult question,
no outside information being available and little personal expe-
rience being obtained.

What we have to consider is the influence of self-induction,
of capacity and of resistance both in the primary and in the
secondary circuit.
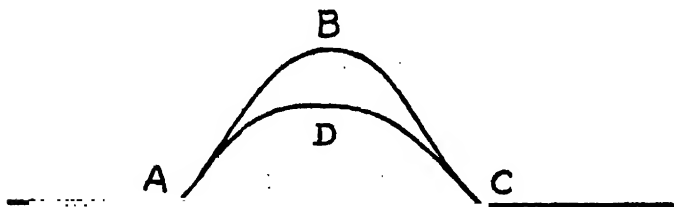
FIG. 28.—Voltage Curve.

Our special way of connecting up so as to make the occurrence
of arcs an absolute impossibility, and the occurrence of sparks
a harmless phenomenon—a point which we shall discuss in a
later chapter—made it rather difficult to judge of the effect of
disturbing influences in the primary, our special arrangements
being made in the secondary circuit.

The intercalation of self-inductance in the primary, outside
the ordinary, proved to be of a very troublesome character;
there is no reason, however, to suppose it would do much harm
in an ordinary circuit beyond the well-known phase shifting.
As we shall learn later, most of the commercial ozonators
are of the dielectric type, which means that the secondary load
of the transformer consists of apparatuses of large capacity,
and the angle of lead may therefore grow to such an amount
that it becomes an absolute necessity to correct it.

We are used to having some self-induction in the secondary load, but so large an amount of capacity is just as strange a load for a transformer. Usually the effect is neglected unless the plant is of such a size as to make proper working an impossibility. A remarkable case of neglect and the result thereof was the following: Somebody had a 5-H.P. motor driving a 3-kilowatt alternator with exciter, feeding a transformer wound for 50,000 volts and an ozonator as load.

Primary tension and current were respectively 100 volts and 23 amperes, secondary tension and amperage were 12,000 volts and 90 milliamperes; the probable power factor was estimated at 0.6, the yield of ozone about 5 gm. per kilowatt hour of secondary energy.

This extraordinarily poor result has to be attributed to the waste of energy in the dielectric, which in this case was made of the wrong material, the enormous quantity of air blown through, viz., about 100 cubic meters per hour, served the purpose of efficient cooling, carrying away nearly all the energy as heat, but that was not the intention of the maker.

Another instance of an extreme case is the system of Schneller, to be discussed later in the chapter on ozonators.

Schneller, in order to avoid (according to his own statement, which, however, is incorrect) the formation of sparks and arcs, joined a high resistance in the circuit. He employed for this purpose glass tubes filled with 80 per cent glycerine, showing an ohmic resistance of about 20,000,000 ohms.

As we shall learn presently, the action of these so-called specific resistances was only for a small part as an ohmic resistance, the chief rôle being the action as a pseudo capacity.

The combined action of self-induction, capacity and resistance in the secondary circuit is of a much more complicated nature than in the ordinary cases, because as we have a discharge through a gas we also have one that is oscillatory in character, and hence very liable to resonance effects and harmonic vibrations, and very sensitive to change of conditions.

As already said, we shall deal with this matter again in the chapter on ozonators and ozonator systems.

g. Influence of Radiations, Magnetic and Electric Fields. After all, the gas would not be a conductor if it were not for the ionizing effect of the discharge itself, and it is easy to under-

stand that the effect of a radiation, be it from radium or any
other radioactive substance, or be it from Roentgen, Becquerel,
Lenard, cathode, or ultraviolet rays, will have the same char-
acter as when we have a discharge going on, but only on a
smaller scale.

Since we may take it for granted that all the enumerated
radiations have some ionizing effect, and since it is known that
as to specific power there is not so much difference between
them, we can speak of the effect of radiation in general, and
not mention the source.

In his book on the conductivity of gases, J. J. Thomson
has so clearly dealt with ionization effects that we wish to
refer the reader to it.

Of course, a discharge will be affected when radiation strikes
it, but in our case, dealing with such powerful discharges, the
effect of any outside radiation cannot be but a trifle of what
its own effects are; it certainly is of no practical value and
solely of theoretical interest to watch the discharge change
upon having radiations strike the discharging space.

A magnetic field acts upon the brush discharge in just the
same way as it does on any other current of electricity of the
same character and there is nothing of interest to be observed
when one has brushes in a magnetic field.

It may be that a very strong field would show interesting
phenomena, but those are not so easy to arrange around a high-
tension discharge of some extension, and we have heretofore
tried only a relatively weak field.

The effect of an electric field, however, is of great importance,
as it is a disturbing agent difficult to control.

It *seems* easy to shield discharges from electric fields, but
they make their own field, and proper grounding is not half as
easy as may be supposed.

Large ozone apparatuses are built of metal and have their
own design, but that also means that the electric fields all around
the dischargers may be of any shape. We can draw simple field
and equipotential lines in a drawing but in actual practice they
seem to run just their own way and that seems to be a queer
one.

Under the heading "influence of spacing of electrodes"
we have already mentioned that a discharge is greatly troubled

by the vicinity of another, unless their distance apart is great enough to prevent interference.

When we do not know how to check the disturbance caused by electric stray fields, the best practical solution of the difficulty is to avoid large metal surfaces and asymetry and to take recourse to larger distances. This is purely practical advice, but the matter is far too complicated to be treated in another way, so much the more as different arrangements create different fields.

All we know about it from our own experience is, that electric stray fields cause a lot of trouble, that they are not easily controlled and that it is best to avoid them. We may remind the reader that we are dealing with large surfaces of metal, high tensions, and great charges, when having commercial ozonators, and that these circumstances are much less controllable than in laboratory experiments.

h. Influence of Dielectric. We now come to the last but most important circumstance influencing the discharge, viz., the question of a solid dielectric between the dischargers proper. This question naturally includes a discussion on the dielectric as such. Any pair of electrodes, no matter of what shape or size, any current, no matter what it is—provided its tension is over a certain minimum, any polar distance, any spacing of electrodes, in short anything is good enough to have brush discharges when one can make use of a solid dielectric between the dischargers.

Not one of the difficulties discussed, present themselves again, but instead of all those, a new one has cropped up—that is the question of the dielectric itself.

Apparently this is what we are accustomed to call a question of material, but now we might draw attention to the fact that indeed very many of-the difficulties in physical experiment, and most of the troubles in technics, are to be classed under the heading of "difficulties of material." If only we could always have a suitable material for some strange purpose! but unfortunately our exigencies go much further than the material possibilities.

In view of the over-important part played by the solid dielectric, we shall have to devote much space to it, for what would be the use of all the advantages of the solid dielectric system if there were no suitable dielectric?

1. DIELECTRICS. A dielectric is a non-conductor, but it has been mentioned already that non-conductivity is to be taken

relatively to true conductivity. When we consider the question very closely it soon becomes evident that there are no absolute non-conductors, though under ordinary circumstances they may seem to be such.

Gases are about the very best non-conductors, but under the influence of the discharge, or rather of the electric charge on the electrode terminals, they change their property of non-conducting, and, as we know, they may, under certain favorable circumstances, be classed as good conductors, even very good ones. So it is with the solid dielectrics, they change their properties under the influence of the circumstances, as for example, heat.

Above the temperature of $\pm 1000°$ C. every substance seems to be a conductor for electricity, there is but one, viz., the nitride of boron, that has been reported to be a fairly good insulator at very high temperatures, and diamond is among those substances that do not change their insulating property but at very high temperatures, much above $1000°$ C.

The literature on the conductivity respectively decrease of insulating power for different materials at very high temperatures is very scant, but it may be expected to grow rapidly in these days of rapid increase of application of electric furnace work.

· That domain need not keep us for the present, although it is interesting just to know that the conductivity or non-conductivity of insulators is in the first place a question of temperature.

We meet this same change at very much lower temperatures for other non-conducting substances, such as glass, porcelain, quartz, etc., and that is what causes the great trouble.

The action of the dielectric between dischargers depends entirely on its non-conductivity, so if it changes in this specific property, the character of the dielectric is lost, there being no non-conductor in that case.

Another difficulty as regards so-called insulators is, that their resistance depends on the applied potential difference and hence is not what we are used to when thinking of metals, when R can be thought of as $\frac{E}{I}$ and does not deviate from Ohm's law until we come to extreme thinnesses in the order of less than one ten-thousandth of a millimeter (0.1μ).

It has been said [1] that the resistance of non-conductors

1. E. T. Z., 1911, p. 622.

decreases with increase of temperature if they are amorphous, and increases if they are crystalline; but those terms amorphous and crystalline are not so sharply defined as they used to be. Modern physics has put an end to a great many *lines* of demarcation and made *regions* out of them with very faint boundaries.

Electric conduction in insulators has to be looked upon as consisting of at least three distinct kinds, viz., the ordinary, the surface and the electrolytic conduction and in addition we have to think of the action of sliding sparks, perforation and destruction by ozone.

Add to these also the question of current, of moisture, of mechanical strain resulting from dielectric stress, and the capacity current in conjunction with dielectric hysteresis, then the more important questions are mentioned, but unfortunately there is very little consistent information about all these points.

Fleming [1] published some highly interesting results as to the behavior of dielectrics when passed by a current.

His conclusions are that:

1. All the dielectrics so far tested prove to possess a true dielectric conductivity for alternating currents, considerably greater than for steady unidirectional currents.

2. This increased conductivity implies greater power dissipation for the same terminal potential difference.

3. The alternating current conductivity increases with the temperature, except in the case of vulcanized India rubber rather below 20° C., and gutta percha rather above 15° C., in both of which cases it decreases with rise in temperature. In the case of mica and very dry paper it is not affected to any sensible extent by rise of temperature over a range between 0° and 60° C.

4. The alternating current conductivity is in most cases a linear function of the frequency, and may be expressed in the form $\varsigma = a + bn$, where a and b are coefficients, which are functions of the temperature, and n is the frequency.

5. The alternating current conductivity, especially that part of it denoted by a, is greatly increased by the presence of moisture in the dielectric. This part is probably identical with the true direct current conductivity.

6. The part of the conductivity denoted by the coefficient a

1. Scient. Amer. Suppl., 1912, p. 45.

is possibly electrolytic in nature, while the part proportional to the frequency is in consequence of an energy loss, which is possibly analogous to the hysteresis loss in iron.

7. The dielectric constant for alternating electric force is in most dielectrics rather smaller than that for steady or uni-directional electric force. In no case is it larger.

8. In the case of pure or vulcanized India rubber the temperature coefficient of the dielectric constant may perhaps be negative within the range of telephonic frequencies and ordinary temperatures.

10. Those dielectrics such as celluloid and gutta percha, which have large alternating current conductivity, although free as far as possible from moisture, also exhibit in a marked manner the phenomena of dielectric absorption and residual charge. .

11. For certain dielectrics there is a temperature at which the power factor and alternating conductivity has maximum values.

Fleming experimented in quite an extensive way with the purpose of investigating the behavior of various dielectrics in low-voltage high-frequency circuits, such as are met with in telephony. His conclusions, however, though relating to that special case are very instructive for our purpose.

To emphasize the complicated nature of the behavior of dielectrics, we will add that very thin films of non-conducting material become conducting under a certain specific pressure, and that some substances such as hard rubber, paraffine, lacquer, become more or less conducting, when exposed to the influence of light—more especially ultra-violet. It is no longer necessary to prove that the question of the dielectric is not a very simple one, and if this material has to be used, one should be prepared to meet a great many puzzling difficulties.

In our special case of the use of dielectric for ozone-making purposes, the problem is greatly simplified by the fact that a great many of the more commonly used dielectrics cannot be considered because the ozone destroys the material. This for example is the case with that large group of rubber compounds, none of which is of any use at all, and we may say that all these fail on account of chemical action.

There is another large group of dielectrics, viz., those of a cellulose fiber base, we mean paper—impregnated or pure—

vulcan fiber, presspahn (pressed paper), pasteboard, and a great many others bearing fancy names. All these suffer from being non-homogeneous and are mechanically destroyed.

The discharge eats its way through these substances unless the material has a considerable thickness. Pressed paper has another peculiar property and that is of allowing a large displacement current to pass, or perhaps better expressed, that it carries a large capacity current, not dissipating any energy in doing so of course, but causing a very large phase-shifting.

These low-resistance dielectrics act as pseudo capacities, and by doing so cause great trouble.

A few of the organic compounds stand the destructive action of ozone. Some lacquers do, for instance shellac, and the new substance known as " Baekelite."

Shellac cannot be obtained in suitable sizes and shapes and has such a low melting-point that it softens too soon; all the lac compounds are destroyed by the action of heat.

Now we may turn our attention to or rather search the mineral domain. Mica is the insulating material most in vogue for ordinary tension work; it stands a fairly high temperature, but unfortunately suffers from being a highly laminated structure. Placed between discharges small parts are continually being peeled off and the heat generated has much to do with this behavior. Mica sheet or tube is soon destroyed. Micanite is little better; it can be used as dielectric between the dischargers but it makes a poor ozonator when it comes to output, reliability and endurance.

Slate is a poor insulator for high-tension work. It is so much of a conductor that in Holland, Prof. Wertheim Salomonson determined the efficiency of Ruhmkorff induction coils by closing the secondary circuit through a pencil of slate and measuring the Joule heat.

The behavior of slate is very irregular, after having been heated for a short time to a high temperature, it no longer conducts. Just *what* causes its conduction is not known yet; probably the oxides of iron and other metals have much to do with it.

Marble and similar substances are poor insulators, their lack of homogeneity being a great drawback. Compressed oxides or other artificially made insulating materials with some

binder are no good, and fall short of mechanical strength unless in very thick strata, so that really leaves nothing to be used but the class of vitrified materials, glass, porcelain, enamel, quartz (silica, vitrosil, etc.).

Glass is a collective name for a large and varied class of material, composed chiefly of silica, alkalies, alkaline earths and oxides of the heavy metals. Speaking in a general way most of the ordinary window and also plate glass is a soft soda-lime silicate, whereas the hard variety is a potash-lime silicate.

Flint glass is a potash-lead silicate.

The potash-lime silicate suits the purpose best of all, but owing to its high melting-point this kind of glass is not as common as the ordinary soft glass.

The trouble about glass is its change of resistance when heated. Now it should be remembered that of all the electrical energy supplied to the ozonator only a small part, at the very most 10 per cent, is expended in making ozone, the rest being dissipated by being converted into heat.

It is this heat that is chiefly responsible for the heating up of the dielectric; there is, however, some work done in the dielectric itself—dielectric hysteresis work—that also causes heat to be generated.

Just at what temperature the graph for conduction-temperature bends appreciably so as to indicate true conduction, is not known, and very likely every different kind of glass will have its own particular curve.

The conduction of glass is for the greater part an electrolytic one, but of a peculiar character. A glass rod heated to say a temperature of 500° C., conducts easily, but to keep it in that condition of conductivity it is not enough to keep the temperature at that point; it has to be raised continually to a higher temperature. When cooled after the first heating one has to raise the temperature to at least 600° C. before conduction starts; after a longer time of rest the original condition is resumed.

This again shows the unstable condition of glass.

A way of well illustrating this property is to use a Ruhmkorff induction coil and two metallic holders for the two glass rods.

When first set to work, the discharge goes from metallic end to metallic end, but on heating the glass rods and having the discharge on at the same time, there comes a moment when the former

discharge between metallic ends contracts itself and now plays between the two glass ends.

This phenomenon is very interesting to watch; it looks rather strange to see a perfect discharge between two glass rods!

The necessity of increasing the temperature of the rods shows itself by the increase of color of the latter, and the electrolytic nature is in evidence by the coloring of the discharge itself in which the sodium coloration is preponderant.

As we have here a case of conduction by means of high temperature the discharge is a flame, as is usual.

The conduction of glass at high temperature is a commonly known fact nowadays, but when the author first started (1895) to find out what might be the cause of the breakdown of glass when placed between discharging terminals there was not much *technical* literature available on this subject.

Now it is known that when we take the specific resistance of sodium glass to be about 5×10^9 at 15° C., it will be about 1×10^6 at about 150° C. and perhaps something like 10 to the first power at 600° C.

Other investigators give 10^{14} as the order of resistance at ordinary temperature, and it seems ridiculous to quote figures in three decimals when the order may be between 10^{15} and 10^{11}.

It is a common mistake of scientific investigators to examine an arbitrary piece of glass and then measure its resistance with great care and accuracy and then say: the specific conductance of " glass " to be 0.101×10^{-14} (G. Fousereau, Journ. Phys., 1883). We can speak of glass as a term for a large variety of certain fused mixtures, but then we should only give approximate or average figures for some property and no decimals with their pretended accuracy! Warburg noted conduction of glass at 200° and 300° C.

The rich lead glasses known as enamels are very poor insulators for high-tension discharges; moreover they are still more sensitive to rise of temperature, which practically means that it takes very little trouble to perforate an enameled plate or a similar substance.

The use of enameled ware for the purpose of dischargers for ozonators has been repeatedly tried by many amateur ozone inventors.[1]

1. The enameled electrodes of the General Electric ventilation ozonators

There are two decidedly differing kinds of porcelain, viz., the so-called French or soft porcelain, and the genuine hard porcelain which originated in China.

The first resembles a glass, in so far as it is a wholly vitrified body, the second is not quite fused but wholly vitrified.

Porcelain, although known for its excellent insulating properties, does not suit the purpose of a dielectric between discharging electrodes, its principal drawback being that it still more so than glass, changes its insulating properties at a rise of temperature. Even at 200° C. it becomes a good conductor and, being so, admits of the passage of such an amount of current that the temperature will increase rapidly, and that of course puts an end to its life, a perforation soon following.

An incidental difficulty is that porcelain cannot be had in the convenient shape of either sheets or strips or tubes of small wall thickness, and anything above about 2 mm. is too thick for our purpose.

Of late, fused quartz or fused silica articles have been developed to such a state of perfection that very much is to be expected from this material, so much the more as experiments in this line have shown that the resistance of it does not appreciably decrease with even a considerable increase in temperature.

Ozonators based on the use of this material, known under the name of " vitrosil ", seem to be in course of construction, and we may hope that in vitrosil the solution of the dielectric problem will be found.

Though the possible use of vitrosil or similar material appeals very much to the author, it must be admitted that some strange statements have been made regarding its use for a dielectric in an ozonator.

2. EFFECT. Riesenfeld said (in 1912) that with quartzglass no brush discharge could be obtained, due probably to its insulating properties.[1]

Now in an alternating current circuit, a non-conductor is no obstacle for the current at all; an ordinary condenser in series in the line does not stop the current but allows its passage through

have their coating as a protection against rusting, there being a glass tube that serves the purpose of dielectric. Of course that is quite a different proposition and an excellent arrangement.

1. Zeit. Electro Chem., 1911, p. 725.

its dielectric displacements. The better insulating property of quartz over glass would only mean that nearly all of the current would be transported through induction and only a very small fraction of it through real ordinary conduction and that would not do any harm to the brush discharge, on the contrary it would assist it.

Warburg [1] gives another explanation of his observation that an ozonator made of quartz gave only half of the ozone. He attributes the loss to the action of ultraviolet light to which the quartz is transparent.

This explanation is not in accordance with the common experience that the influence of ultraviolet light (by the way, there is not so much of this in the brush discharge though it looks violet!) has no appreciable effect when we have to do with regular *commercial* ozonators.

The effect of ultraviolet rays belongs to the domain of physical experiments and should not be called upon to explain a decrease in output of 50 per cent.

It is difficult to explain other people's mistakes, but it seems very probable here that the halving in output is rather due to increased ressitance when using quartz of the same thickness as glass, the first taking more voltage to have the same current flow.

Although the modern glass industry is capable of supplying all kinds of glass if there is a demand for some special kind, and although in the later years different ozonator manufacturers seem to have overcome the trouble from breakage by a careful choice of the material, still it would indeed be a great boon for the ozone industry if it were possible to have a material that was still better than the best glass.

We look forward to vitrosil with great confidence as we also do to Baekelite; unfortunately our own experience has not been extended over these materials that are of a more recent date than at the time at which our experiments were made in Holland.

The next best thing to prevention is cure, and if heat destroys the dielectric, and if we cannot prevent that heat, then the best way out is to try to carry off as much of the heat as we can. That is a question of ozonator design. As said before by far the most of the energy supplied is wasted as heat, and we can-

1. Ann. d. Phys., 1909, V. 28, p. 17.

not help that, since that lies in the nature of the discharge, but it is quite feasible to keep the apparatus at a certain temperature of equilibrium through artificial cooling, either by air or water.

The best we can do of course is to keep the dielectric itself at a normal temperature, but that is rather a difficult proposition, and the regular way is to cool the electrodes, or one of them, and by doing so carry off the heat from the dielectric.

The well-known firm of Siemens & Halske of Berlin, pioneers in the line of ozone, have succeeded in cooling the dielectric itself in a very efficient and ingenious way. They use the cooling water as one electrode and have it circulate round the dielectric; this certainly is the most direct way of cooling it, and judging from their large practice it is evident that their method gives perfect satisfaction (see later chapters on ozonators, etc.).

It may be well to call attention to the fact that the breakdown of a glass dielectric in ozonators is not due to the perforating power of the tension but to the conduction of a heated spot.

The wall-thickness of ordinary ozonator glass is about 2 mm., and it would require a potential difference many times that applied, in order to really perforate it.

This is an interesting question, far less simple than might be supposed or concluded from such statements as: " it takes 30,000 volts per millimeter thickness to perforate glass," that is only a very rough approximation.

Moscicky,[1] who for the sake of knowledge how to construct commercial high-tension condensers, experimenting in the line of dielectric perforation, stated that one of the first things to discriminate between, is, whether the electrodes are concentrated in the middle or spread all over the surface. It takes for a glass of $\frac{1}{2}$-mm. thickness, a little over 11,700 volts in the latter case, and over 67,000 volts to perforate with electrodes only in the middle.

Another point is the influence of frequency. It seems that a higher frequency greatly favors perforation or permits of this at a very much lower tension.

In actual work with ozonators using one dielectric, the tension is seldom very much more than about 10,000 volts or 12,000, sometimes as low as about 6500. Gerard uses 25,000 on his

1. E. T. Z., 1904, p. 544.

double dielectric, but Otto (Abraham Marmier) does not use more than 12,000 on their double dielectric ozonator.

Evidently all these values keep well away from the perforating tension, considering that the usual wall thickness is about 1–2 mm.

The value for perforating tension does not come in for recommendation of some dielectric; it is always high enough.

That for vitrosil seems to be about 30,000 volts for 1 mm. thickness. The graphs for thickness of dielectric in function of perforating voltage given by Moscicky are straight lines, but Zipp says[1] that perforating pressure is not at all proportionate to thickness. This experimenter draws attention to the influence of time of duration of applied force.

A dielectric that may hold several volts for an indefinite period may resist double the amount for a short time, and that is the common experience when testing insulating materials for their insulating properties. The factor of time is a very important condition to be settled beforehand.

Over and over again the factor of time is forgotten when considering phenomena that apparently have nothing to do with time.

So with reference to a discharge, it is generally overlooked, that at transient voltages of limited energy the striking distance is a function of the energy but not of the voltage.

3. ARRANGEMENT. As said before it matters very little now in this case of a dielectric, what shape or size the electrode terminals have, but we can have differences in the ways the dielectric is applied. In Fig. 29 we give the different possibilities that are in use; in A we see one air space and one dielectric, in B we see two air spaces and one dielectric, in C we see one air space and two dielectrics, while in D is shown a modification patented by Siemens in 1891 but never used.

It does not make any material difference in the working how the air space and dielectric are arranged; it is merely a question of preference of construction, and we shall refer to these arrangements in a later chapter on ozonator design. All these are in actual use.

An important point to be considered when using dielectrics is the enormous amount of capacity they give in the secondary

1. Zipp, Hochspannungs Technick.

circuit, and for a transformer that is just as unpleasant a load as is self-induction, but it can be corrected and should be when
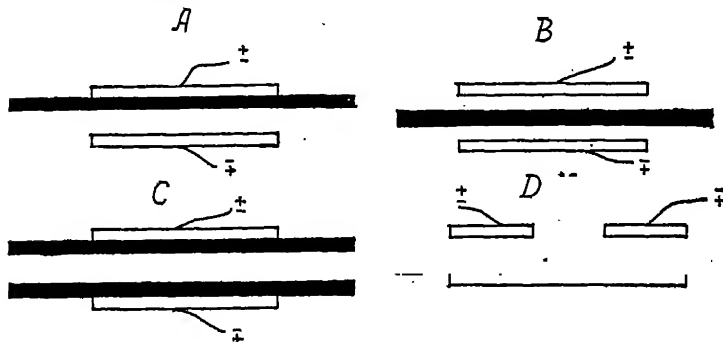

FIG. 29.—Different Positions of Dielectric (in black).

we have to think of application on a large scale. Gray[1] called attention to the fact that the capacity of an ozonator changes
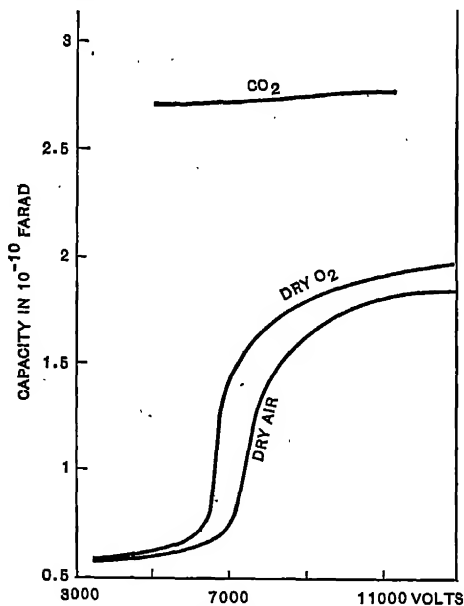

FIG. 30.—Voltage-capacity Curves.

when it is working, that is to say there is a steady increase in

1. E. T. Z., 1905, p. 518.

capacity on increasing the current strength that is passing until
a certain point is reached.   It also depends on the gas.

Gray gave some very interesting graphs which we show in
Figs. 30, 31, 32.

There is a very marked difference for carbonic acid and for
air or oxygen, but not much for these latter two, and there will
probably be hardly any difference at all when we take ozone
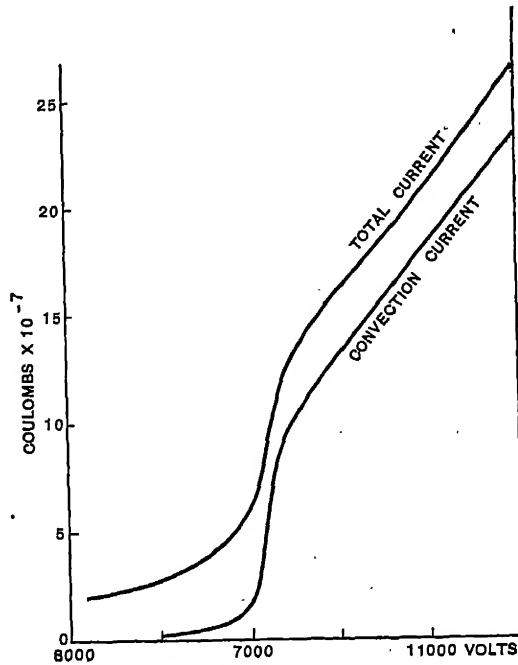instead of air, for the ozone is only ozonized air.   He also

FIG. 31.—Voltage-current Curves.

showed that the total current taken by the ozonator is made up
of the sum of the current for " charging " and that for passage;
see Fig. 31.

In glass the first usually does not exceed 1 per cent of the
total, but with other dielectrics it may be considerably more and
cause great trouble on account of its phase shifting.

The practical result is that for the making of ozone there
actually is less current or rather energy taken than is indicated

by the product of volt and ammeter readings. The graph in Fig. 32 is after Gray; it is a pity he worked on so small a scale.

When having a dielectric we can have discharge from a strip or plate, but it is interesting to know that from polished surfaces the discharge does not start unless the potential difference is raised considerably above that which is needed for rough surfaces when the electrodes are at the same polar distance. There is no advantage to be gained by having very smooth sur-
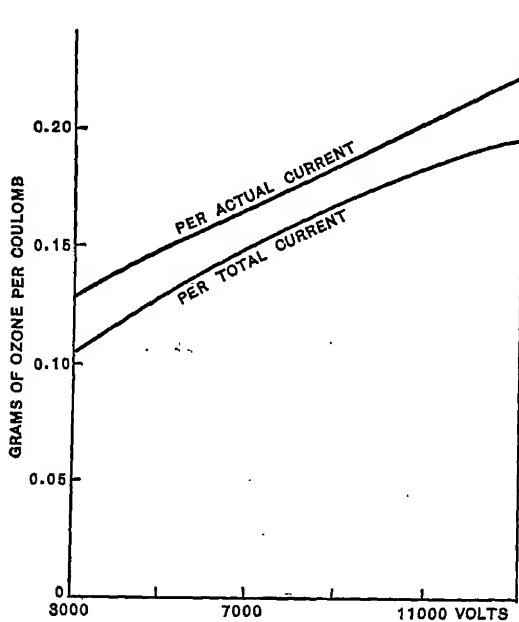

FIG. 32.—Output-voltage Curves.

faces; that is why some people prefer to take fine wire gauze instead of plane surfaces.

There is much to say in preference for one sharp-edged discharger. Here again only because there is so much less tension required to produce the discharge.

The theoretical explanation as to why a solid dielectric suppresses the spark, or to express it more strongly, why it should make any other discharge but the brush an impossibility is not yet given.

The flame and the arc discharge are true heavy-current discharges, and these cannot take place in a circuit of high resist-

ance, but the spark is not so far away from the brush and it is not evident why this spark cannot exist when a dielectric is placed between the discharges.

It may be mentioned that from the brush, only the stem is to be had, the aigrette does not occur, and that is just why the brush in this particular case is so much more efficient with reference to the production of ozone, it being the stem that is the more active. This also explains why smaller polar distance is beneficial to ozone production, but we could not have that small polar distance if there were no dielectric between the electrodes.

It is customary to have no more polar distance than say 2 or at the most 5 mm. We have mentioned that under the best conditions and with ordinary frequency current, 7 mm. was the least and practically one had to take about 13 mm. when not using a solid dielectric
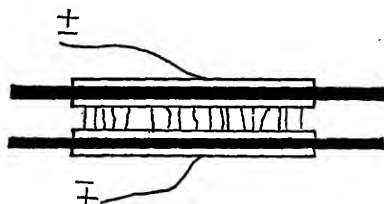

Fig. 33.—Special Arrangement of Dischargers.

A curious experiment is to take two dielectrics and a second set of electrodes inside, so that the circuit is made up of a metal, glass, metal, air, metal, glass, metal; under these circumstances there is no brush discharge, but quite a number of tiny little sparks, straight lined and rather unlike the ordinary sparks. See Fig. 33.

It is questionable whether it is more advantageous to have a space between electrode and dielectric or have them stuck together say with shellac, to have the metal electrolytically deposited on the glass, or adhering according to the Schoop method. Personally I am in favor of placing the dielectric close to but loose from one electrode when they are unlike and in the middle when they are similar.

It should be borne in mind that if there is perforation of the dielectric the flame will set up and thereby ruin the apparatus, melting anything that is in the way, glass, metal and all; that flame short circuits the transformer and should by all means be guarded against.

CHAPTER X

THEORY OF BRUSH DISCHARGE

AMONG all theories on electricity, the discharge from points, known as the brush, forms one of the most trying problems for satisfactory explanation. The more common view, that the actual flow of electricity is composed of a current of electrons, does not very well fit in with the fact that it is not the negative but the positive electrode which gives the true brush.

A double layer has to come to help us out of the trouble about a flow from a deficit, and the electrical wind as observed, or rather experienced as a pressure, will have to be accepted as something else.

Double layers are a handy method of " explaining ", though most people do not quite grasp the meaning. They are said to arise from a film of condensed gas with a negative charge inside, close to the electrode proper, and a positive charge outside, these double layers helping to pull the corpuscles away from the metal.

The brush discharge has always been a difficult problem to handle for scientists, even H. A. Lorentz admits that and we are very much surprised that this very interesting and fascinating discharge has received so little attention from scientists.

The trouble is that we might say that from a positive point positive electricity is discharging, but we cannot very well say that from a positive point negative electrons are driven out; unfortunately we do not know of positive electrons.

To admit that the discharge is being caused by the inward rush of electrons and attribute the outward flow to a double layer is one thing, but it is quite another to explain the configuration of the brush and the actual wind direction. We have always considered the brush discharge to be a continuous discharge and not oscillatory in character, but Kabakjian's contrary statement seems conclusive, his oscillographs being very convincing indeed.

Kabakjian [1] has taken oscillographs from brush discharges with dielectrics; it is a pity he did not also take these from true and free brushes playing between electrodes without the intervention of a dielectric.

He says that it is not easy under ordinary circumstances to obtain steady discharges in that way for any length of time, as the high state of ionization of the air and also the vapor of the electrode material facilitate the passage of a spark or the formation of an arc between the electrodes.

We never experienced the slightest difficulty in maintaining a true brush discharge between electrodes in free air for any length of time provided the voltage was kept fairly constant and the electrodes free from dust.

His conclusions [2] are as follows:

1. The silent (brush) discharge obtained by alternating current and a dielectric, is under certain circumstances oscillatory in character.

2. Increase of capacity or decrease of air space tends to decrease the amplitude, giving rise to smoother discharge current curves.

3. Variations in current density or the insertion of a 33,000-ohm resistance do not affect the shape of the discharge curve.

4. Moisture in the air diminishes the value of the discharge current for a given voltage and air space, the discharge loses its luminosity and there are more isolated points and tiny blue sparks scattered all over.

The intersection of a dielectric between the electrodes materially changes the character of the discharge, so it may be that, after all, the free brush is not oscillatory like the other.

As soon as there is a dielectric there is no more of that peculiar spreading out at the base, and it is rather difficult to make a mental picture of an oscillatory brush. We most sincerely hope that Kabakjian will extend his research to free brushes.

Recapitulation. The complexity of the discharge makes it difficult to remember all the different phenomena and yet it is of much importance that one should distinguish between the different discharges and their different effects.

Glow discharge and corona are characterized as being high-

1. Phys. Rev. (31), 1910, p. 117, 122.   2. Phys. Rev. 31, l. o.

tension discharges of little energy, both being rather independent of electrodes and not so very sensitive to change of circumstances. All this in comparison with the brush discharge, characterized by its peculiar noise, its blue-violet color, its gentle flow, the accompanying of the so-called electric wind and above all by its remarkable power of converting oxygen into ozone.

It is high-tension discharge, from the positive electrode unidirectional except under special circumstances, when it seems to be not a steady but a wave discharge.

The brush discharge is very sensitive to change of conditions, and also to shape of electrodes, a point or a sharp edge being essential for the free brush when the counter pole is near by.

The amperage may be fairly large; it is at its best at ordinary pressure, ordinary temperature and medium high frequency.

The spark discharge is characterized by its loud snapping noise, its violence, its yellow color and its oscillatory nature. The spark does not generate ozone, but does cause some nitrous compounds to be formed; it is a high-tension low-amperage discharge of great perforating power; it is the result of accumulated electric charge and hence starts best from large-sized spheres or curved planes.

The flame and arc discharge are essentially low-tension phenomena, being characterized by the large amperage and large energy. The flame generates some nitrous compounds in air as does the arc. Both are known for their very high temperature, the arc being a controlled flame. Both are very sensitive to magnetic fields but are little affected by the kind of electrode.

As regards the influence of conditions, the more important are temperature, pressure, and electrodes; while the intervention of a solid dielectric between the dischargers changes the conditions so materially as to give rise to new behavior. In case we have a solid dielectric between there is no chance whatever for a flame or an arc discharge, these heavy amperage discharges cannot exist in a circuit of that kind, neither can a spark and the only chance for discharge is as a brush. This brush is also changed in its character in so far as it has lost much of its individuality, its pronounced "will" so to say. It has become tamed but fortunately it has kept its valuable property of converting oxygen into ozone.

CHAPTER XI

OZONATORS

a. No dielectric. There are two classes of ozonators, viz., those based upon the principle of the use of a dielectric between the dischargers, and those that do not use a dielectric except of course the air itself, which can hardly be called such.

Let us first see what systems are, or rather have been used, to get rid of the dielectric troubles.

Since Werner von Siemens built a small commercial ozonator in the year 1857 every worker in that line has been using the principle of a dielectric between dischargers, so as to have the brush discharge, and be guarded against sparks, flames and arcs, but in the year 1894 Schneller took out a patent for an ozonator using no dielectric at all and aroused the interest of many scientists, some of whom paid a visit to the experimental plant of Tindal in Holland, where the Schneller system was being investigated. (We mention this because some people call it the Tindal system, or later the de Frise system.)

1. THE SCHNELLER SYSTEM. Schneller looking upon the dielectric between the dischargers as some kind of resistance, thought that it would be possible to place it somewhere else in the line, and then replace it by something else at the same time; so he took a liquid as resistance, viz., a glass tube filled with an 80 per cent glycerine and placed that in the circuit as indicated in Fig. 34.

From the high, at that time, very high tension transformer (50,000 volts) one terminal was connected to earth as was one terminal of the ozonator.

The other terminal wire led to the tube of glycerine about ⅜ in. diameter and about 2 ft. 6 ins. in length and from there to the discharger proper, being very fine platinum wire gauze clamped on edge between brass strips so as to provide for a great number of fine points.

Schneller's first 2000-watt apparatus contained 75 of these tubes in parallel, each holding a strip of platinum wire gauze of about 20 cm. in length, discharging from both sides.

The 75 were arranged in five sets of 15 and each set enclosed in a casing.

The air, after having been ozonized in the first compartment, had to pass a refrigerating compartment, kept at minus 25° C., before entering the second, and so on until the fifth.

The total length of discharge was 75 times twice 20 cm. or 15 meters for a 1-kilowatt discharge. This is a rather high figure. The polar distance of 30 mm. was the main reason for the very low efficiency.

In Fig. 35, the apparatus is shown in sketch, the general arrangement being easy to understand and needs no special drawing.

The system as such was a perfect failure, but at that time it surely had the merit of novelty and of being pioneer work; when once somebody has proven a generally accepted statement, in this case the necessity of a solid dielectric, to be wrong, it is easier for someone else to continue research in that line of deviation.

Fig. 34.—Schneller System.

That credit should be given to Schneller. He pointed to a new line of departure, took a totally wrong step himself, but in the meantime gave someone else a chance to avoid the mistakes he had made.

At that time many scientists took interest in Schneller's work, and many faulty explanations have been given.

The fallacy of the system was proven when the attempt was made to substitute some other material as a resistance material, because glycerine gave much trouble.
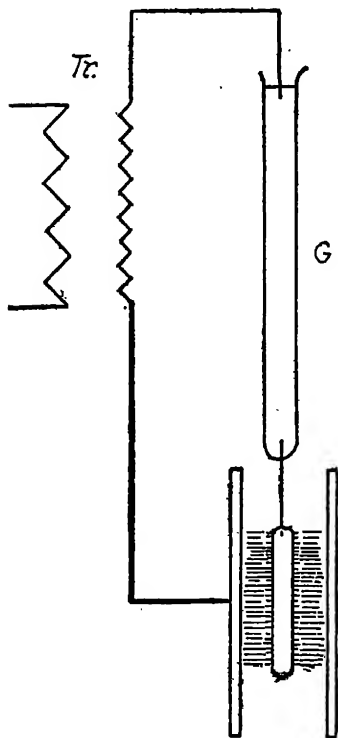
It seems such an easy problem to find a suitable substitute for the liquid resistance, and although there are so many and such a variety of insulating materials, there is not one among them all that suits the purpose.

Physicists often use lead-pencil lines, drawn on frosted glass, but that is of no use at all when dealing with high-tension cur-
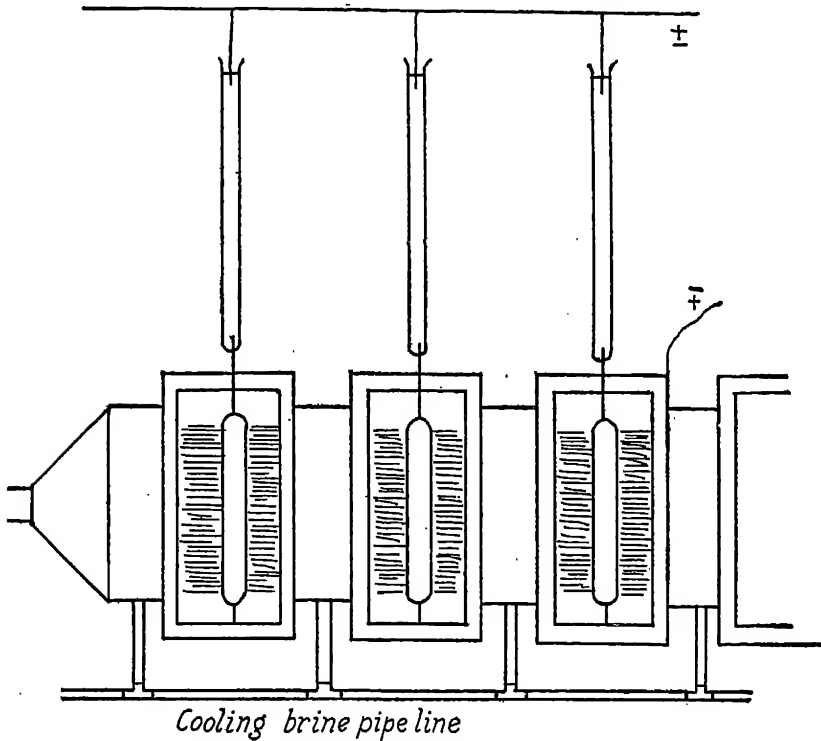

Cooling brine pipe line

FIG. 35.—Schneller (Tindal) Ozonator.

rent, which jumps along it and the effect is zero. Similar negative effect is obtained when using powdered metals or oxides.

Schneller himself proposed porous earthenware known as biscuit, but that only works as long as there is enough moisture in it for it to conduct, and within ten minutes that has dried away.

The only substance that was of any use though only to a very small extent, was slate.

The author tested nearly every substance that can be thought

of in this line, but none did the work. The examination gave rise to many an interesting observation, but no material was met with that could be used.

It should be borne in mind that we were looking for a resistance of about 20,000,000 ohms and capable of carrying say 100 milliamperes. That brings metallic resistance out of the question on account of prohibitive cost.

A long series of experiments along this line at last demonstrated that the action of Schneller's so-called specific resistance is not that of an ohmic resistance but that of a pseudo capacity, and this explains why neither spark nor arc is excluded, though this is claimed by the patentee.

The tension had to be watched very carefully so as not to exceed the normal; if it did, sparks became more and more numerous and finally the " resistance " gave way and an arc resulted.

They never tried it, but the system might have worked just as well without the " resistances " in the circuit, as they never knew what was going on, not having the laboratory outfit to investigate the matter thoroughly. It has taken the author a considerable time to arrive at these conclusions, but his experimental laboratory was equipped for the purpose of research and the scientific end of the problem was very fascinating.

Some years later Schneller took out a patent for an enamel coating on one of his electrodes, but did not call it a dielectric and said it served the purpose of a smooth surface!

2. THE TELSA SYSTEM. When we remember the change brought about by having high-frequency discharges and in the first place think of the difficulty for a spark to form, and the preference for brushes, it will not surprise us that Tesla also took out a patent for the manufacture of ozone by his famous high-frequency discharges.

As said before the discharges are quite a sight to behold, but when it comes to ozone making there is nothing but disappointment, the output being hardly worth while speaking of in comparison to that of other methods.

There have been some ozonators on the market, based upon this principle, and used for the purpose of ventilation. The noise of the air-gap spark, now known to everybody from the wireless telegraphy, is a drawback for many people, and as better

apparatuses have been put into use and proved a success there is no need any more for the Tesla system in the ozone business. In Fig. 36 we give a diagrammatical sketch of the Tesla system which, however, can be simplified to Fig. 37 without interfering with the action. The air-gap is essential for obtaining high-frequency discharge.
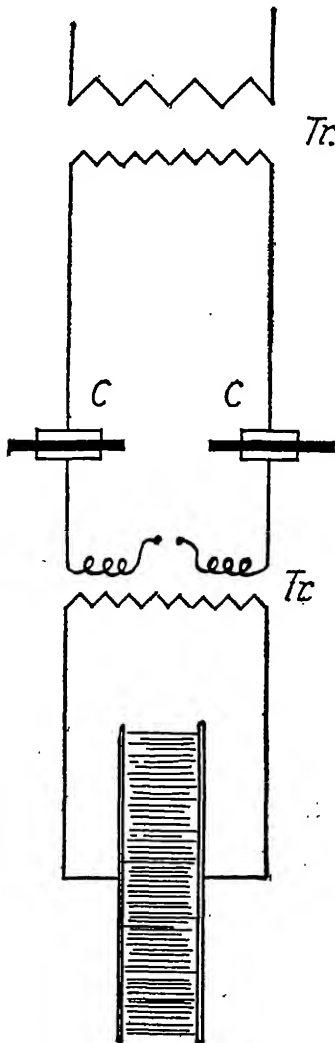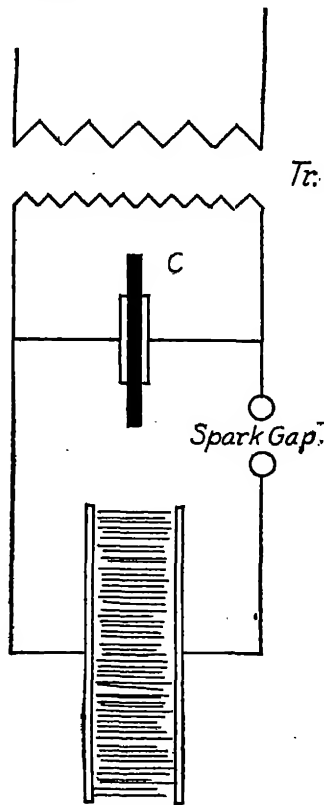
FIG. 36.—Tesla System.   FIG. 37.—Tesla System.

3. THE OTTO SYSTEM. Otto, recognizing the well-known fact that an electric arc can easily be extinguished when we only

increase the distance between discharging ends, arranged his
electrodes in such a way that there is relative displacement of
one with regard to the other.

This means practically that one electrode, or a number of
them, rotates inside or outside a fixed counter pole. When an
arc has formed, the same is drawn out by the relative displacement
of the discharger, and if it intended to form, it cannot do so
because before having made up its mind, the accomplishment
has been made impossible by the increased distance.

In Fig. 38 we give a diagrammatical sketch of the idea, good
enough in itself but evidently not constructed in the right way.
The Otto revolving ozonator has not been a success.

If Otto had kept in mind the wave form of the discharge,
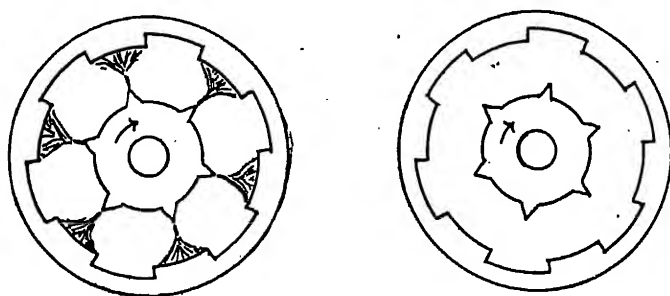and realized that in order not only to prevent but to avoid arcs

FIG. 38.—Otto Revolving Ozonator.

altogether, the motion of the revolving discharger should syn-
chronize with the periodicity of the current the system might
then have given better satisfaction.

It is not enough to extinguish an existing arc, it should be made
an impossibility to start, and that could be done, provided there
was harmony between rotation of dischargers and periodicity
of current.

4. THE VOSMAER SYSTEM. If we look upon the brush dis-
charge as an individual kind, having its own laws and by-laws,
there is no need for any special arrangement preventing other dis-
charges. It is better to do all we can to provoke the brush itself,
and one should not bother about other kinds of discharges.

The first necessity of course is very sharp dischargers
proper for one electrode, flat surfaces for the other, and that is

all as far as the principle goes. There is no difficulty in maintaining the discharge as brushes as long as there are no seriously interfering disturbances such as accidental rise in voltage, or particles of dust or metal.

After having made a 1000-watt ozonator in such a way that the discharge could take place under most favorable condition, it was experienced that some safety arrangement had to be applied so as to be able to leave the apparatus without any attendance, and as this safety appliance is in itself a thing of interest, it may be discussed here at some length.

In Fig. 39 the circuit is shown; here Tr means an ordinary transformer, L is a self-induction wound for high tension, C is a high-tension condenser, and O stands for the ozonator.
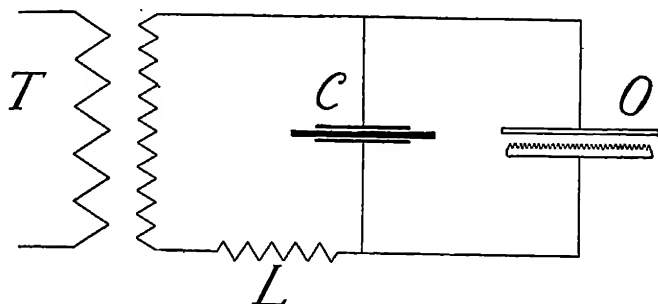

FIG. 39.—Vosmaer System.

The combined effect of self-induction and capacity is: a remarkable rise in voltage. Suppose the transformer is supplied with 110-volt, 100-period alternating current, and let the ratio of transformation be 1 to 70, then if there were no L and C the secondary tension would be ±7700 volts, but now in this particular case, with given values for L, C and the resistance of O, the secondary potential difference between the terminals of the ozonator is 10,000!

Said *rise* of tension from the regular 7700 to the special 10,000, is due to the combined effect of L and C, in conjunction with the R of the ozonator. If this resistance in the ozonator drops, the *rise* also drops.

Now suppose there is some reason why, in the ozonator, there be a disturbance of the stationary condition—pseudo

equilibrium—say a particle of metal or dust between the dischargers, then a spark will try to start, the particle of dust forming a suitable vehicle for a larger current, but as soon as that is the case, the resistance at O falls off, a spark being a discharge of less resistance, but if this happens, then the potential difference between dischargers decreases and does so to a point where it is not enough to gap the polar distance. In this way the spark through its own birth also checks its own conditions for existence, and only when the tension be raised artificially by means of increased primary tension is it possible to have some sparking; the rest of the discharging points, however, go on with the brush as if the sparks were not there. When the tension is raised intentionally by say 20 per cent, the sparking is heavy, but not disturbing, and the most important fact is, that it is an impossibility to obtain a flame or arc discharge, the nature of the circuit arrangement not permitting that.

As long as the primary tension is fairly constant, there is no danger of excessive sparking, and the system can be left to itself without any attention at all. We used to leave it for hours and hours and never in all the years of work had any trouble with it.

In the laboratory we tried to see how far that rise in tension could be pushed through ordinary means, and so we succeeded in obtaining the standard 10,000 volts with a primary tension of no more than 11 volts. The effect of the special way of connecting up evidently being that instead of 770 volts there were 10,000 at the end of the terminals of the ozonator!

The larger the ozonator, the smaller the sum total of resistance as resulting from all the air spaces in parallel, the larger the product $L \times C$ has to be.

It is immaterial how the product, capacity $\times$ reactance, is obtained, but for practical reasons it is preferable to have it in such a way that there is not very much phase-shifting.

In the year 1902 when the author took out a patent for this special way of connecting up, there were no commercial high-tension condensers on the market (in Europe), and it has taken some time before that problem was being satisfactorily solved. We made plate glass in oil condensers, and for instance had some difficulty in getting over the trouble of skin effect, and also air bubbles. There would be no such difficulty in the present

state of advanced technics. Though improvement on this system is not impossible, still it is hardly to be expected that it ever will be able to compete with the system based upon the use of a solid dielectric between electrodes, the yield in grams of ozone per kilowatt hour being so much higher in this latter case.

The Vosmaer system, though worked out with great perseverance, investigated with scientific knowledge, and tested on a large scale experimentally and practically, has had to undergo the same fate as all the other attempts to go round the dielectric. Neither this, nor the Otto, nor the Schneller nor the Tesla system has succeeded. We all have had to confess the superiority of the older and much improved upon system of using a dielectric. Fig. 39a gives an outside view of a 2000-watt ozonator.

b. **Dielectric Systems.** That word system in plural is rather a misnomer; the hundred and more patents taken out for ozonators, using dielectrics should not be called *systems*, as they are all based upon one and the same principle. Their difference, if they do differ at all, lies in details of arrangement, generally of very little importance indeed, but considered a great novelty by their respective inventors.

We shall deal with them briefly.

We have already mentioned that it is immaterial for the discharge as such, how the electrodes are made; it is only a matter of detail whether they are made of plane plates, strips, spheres, points, or edges; it does not matter whether they are arranged spirally, straight, or inclined, or such like fancy forms. Some people take wire gauze, others wire, some use powdered metals, others use smooth-surfaced electrodes. Some take two like electrodes, others have one differing in shape from the other; in short there is a great amount of apparent diversity, but about 95 per cent of the patents have never been in actual use on a large scale, and are not worth much attention.

It is only a matter of taste whether we prefer the tube arrangement or the plane, either as strips or as planes of dielectric.

Details of construction may give special advantages of cleaning or repairing.

Let us take some examples: suppose someone wishes to arrange discharges and dielectric as per Fig. 29a, then someone else comes and substitutes solid plane metallic plates for plane plates but hollow, so as to allow cooling water to circulate through, to keep
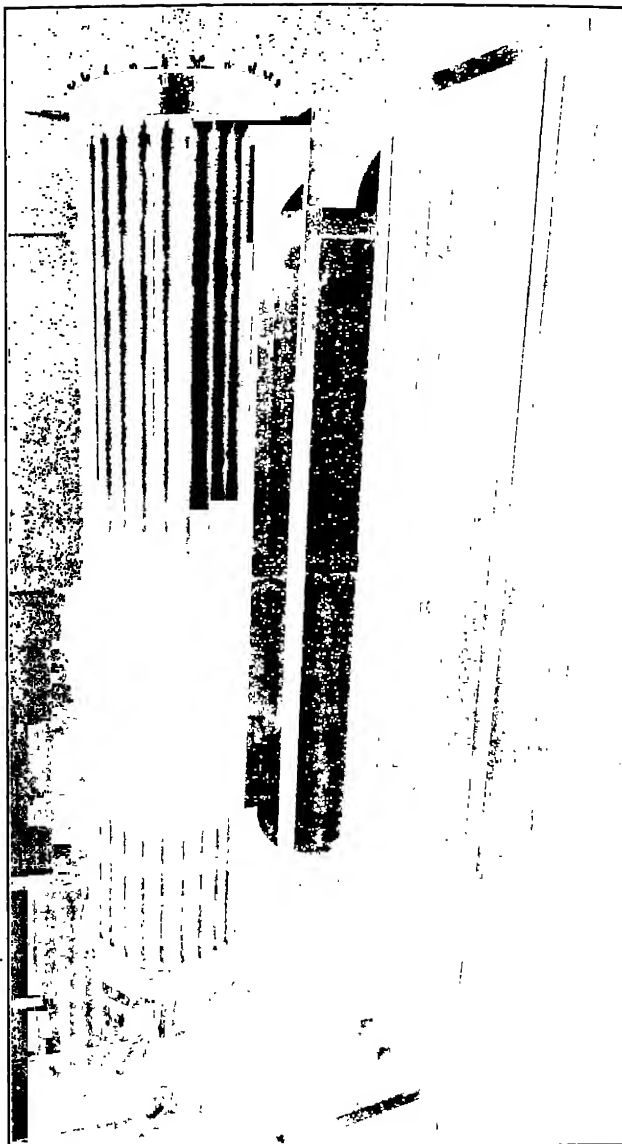
FIG. 39a.—Vosmaer Ozonator (old style).

electrode and dielectric cool; now that is another patent though there is nothing new about it at all.

Someone makes an ozonator from a glass tube, one metal cylinder inside and another outside, then someone else comes and inserts a second glass tube coaxial with the other cylinders,
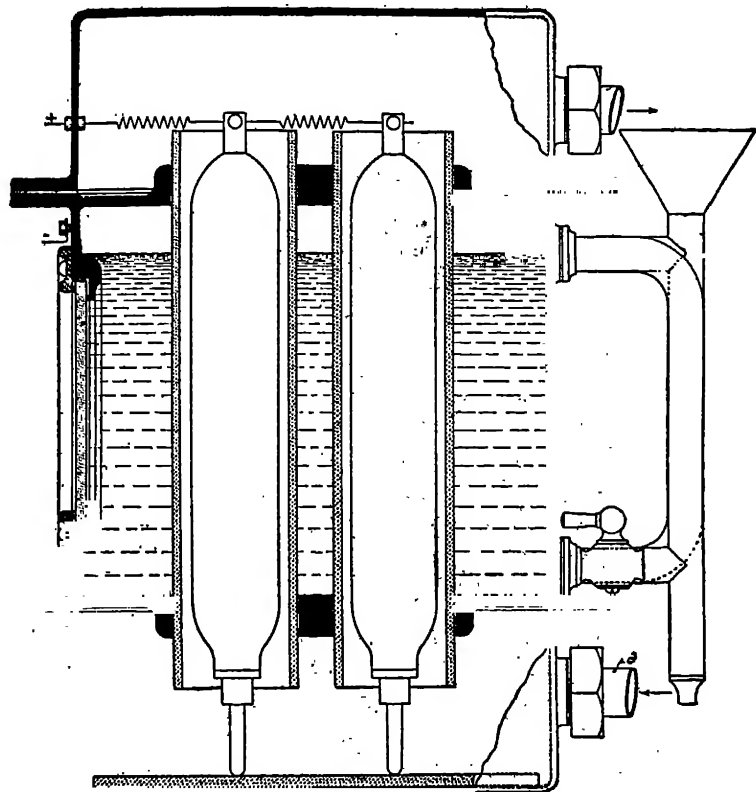

FIG. 40.—Siemens-Halske Ozonator.

then that is another patent though actually there is nothing new, no inventive genius being needed to think of that change. One man patents the use of a wire wound spirally around a tube, another places the spirally wound wire inside!

As we shall see in the chapter dealing with the uses of ozone, there is a demand for very weak ozone, there is one for a strong and one for a very strong concentration, accordingly there is a

demand for different styles of ozonators. Some have to be efficient before everything, others again ask for reliability first, and there is also a place for ozonators of low output but of great simplicity.

There are cases where efficiency is of no importance at all, and a fool-proof make of primary importance, and so there is place for widely different styles of ozonators, though they all belong to the same *class* as regards principle of operation.
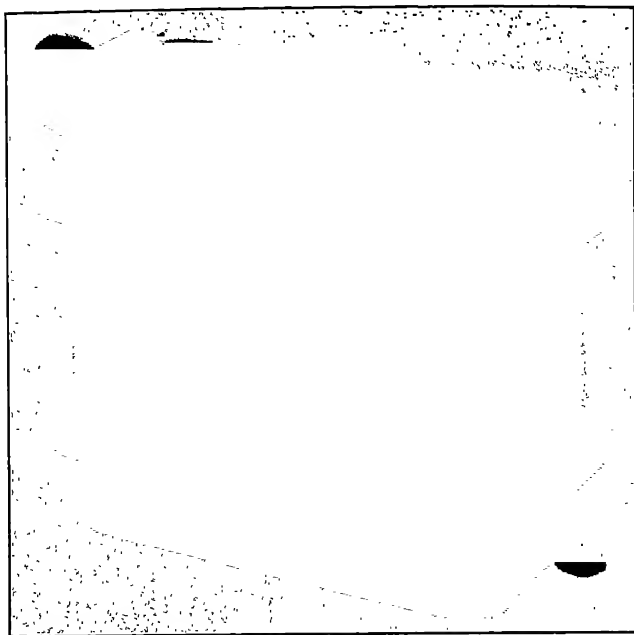
FIG. 41.—Siemens-Halske Ozonator.

So it is that details of construction may be of more importance even than a principle, but we should not consider the constructor as an inventor. A *well-made* apparatus is *not* an *invention*, but a result of practical experience.

1. SIEMENS AND HALSKE. Siemens has been working in the line of ozonators since 1857, but not until lately has he succeeded in making a good, probably the best ozonator for the present.

Between 1857, the year of the first Siemens ozonator, a small

glass tube arrangement, and the year 1890, very little headway was made in the line of ozonators, not even by the firm of Siemens & Halske, but then they started, and in 1891 their Dr. Froehlich gave a lecture on ozonators before the German society of Electrical Engineers (published in Electrotechnische Zeitschrift, 1891). In those years there was lively activity in this matter in different countries, but through all the attempts to improve upon the system, the old Siemens dielectric system held its own and improved itself.

The firm tried mica tubes, glass tubes, panes of plate glass, and finally brought out the tube of glass with an inside metallic electrode and an outside liquid electrode. This type has
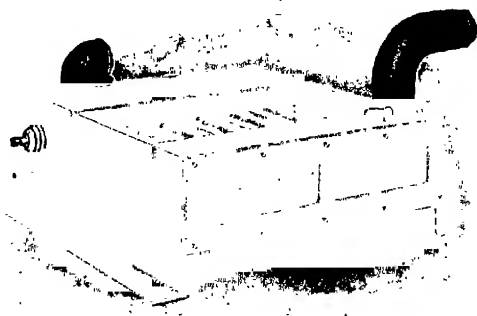

FIG. 41a.—General Electric Co. Ozonator.

become their standard for the present time and is in actual use on a very large scale in many different places all over Europe so that it is fairly safe to consider this a success.

The troubles from breakage of the dielectric seems to have been overcome by a careful testing and selection of the tubes, and occasional breakage is neutralized by simple construction so that renewal of dielectric is possible without too much trouble.

In Fig. 40 we give a sketch of the apparatus which is shown in Fig. 41. One unit generally contains eight tubes but the new horizontal type seems to have no more than six.

2. GENERAL ELECTRIC. In general make quite similar to the Siemens tube, is the industrial or laboratory ozonator of the General Electric Co. There are six tubes joined to a unit, encased in a cast-iron box and placed horizontally. The inner electrode

is not an aluminum tube like Siemens uses, but an enameled
iron one; the outside electrode is the cooling water and these two
electrodes are separated by the usual glass dielectric.   The whole
is a very handy and neat out-
fit as shown in Fig. 41a and b.

3. GERARD.[1]   There is an-
other type which should be
mentioned although it does
not seem to be very much in
use.   Its advantage is the high
output and high concentration
of ozone, its disadvantage is
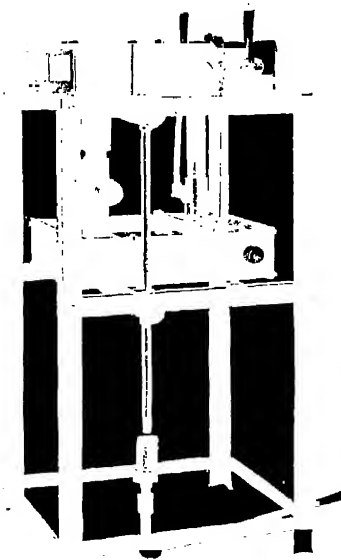its costly renewal when a
breakdown occurs.   It is the

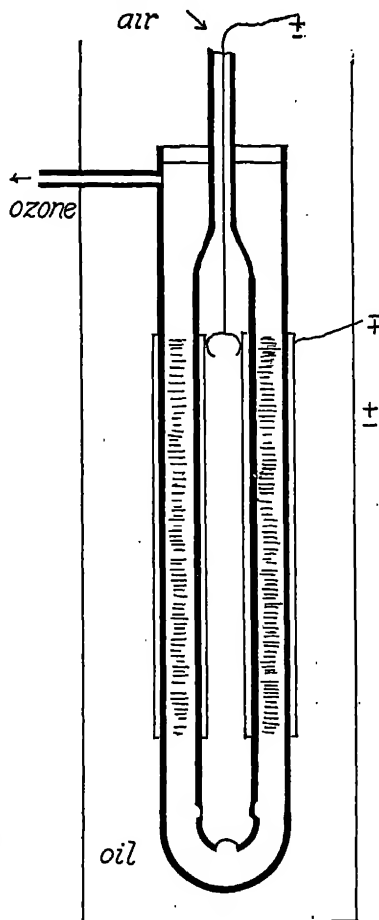FIG. 41b.—General Electric Co.
Ozonator.

FIG. 42.—Girard Ozonator.

Gerard, formerly a very long tube, but later shortened so as
to become less awkward.   In Fig. 42 we give a sketch of the
principle; here we see the use of a double dielectric instead of

[1] Manufactured by the Westinghouse Co.

a single one; this certainly causes much more resistance for the discharge, but the result seems to be in favor of concentration.

This Gerard tube is the practical outcome of the old original Berthelot tube, and seems particularly adapted for laboratory and experimental use. It might have been developed to a commercial apparatus, but for the present seems to remain dormant.

4. SMALL-LINDER.[1] Another type is the Small-Linder grid apparatus, see Fig. 43. This also has not been developed to
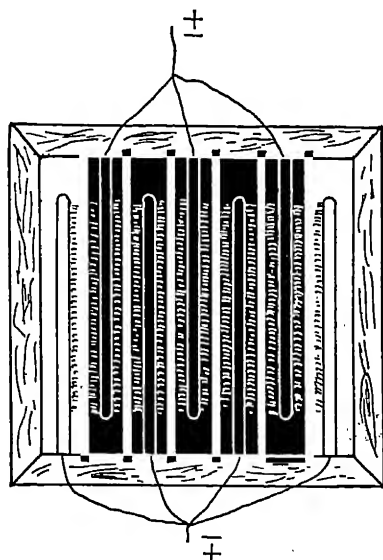

FIG. 43.—Small-Linder Ozonator.

the extent it should have been; it is a promising arrangement and seems well suited for certain applications; it is not made for very high concentrations but will answer the purpose for most of the applications of ozone. Fig. 44 is a cut of the apparatus when at work.

The diagrammatic sketches seem simple enough to be understood without further explanation. An advantage of the Small-Linder type is its cheapness of construction, and the ease with which repairs or renewals can be carried out.

Suppose accidentally a glass strip breaks, at very little cost and trouble a new one can be put in.

1. Also called Vohr and manufactured by the Hudson Ozone Machine Co.

There is, however, no possibility of efficient cooling, so that the amount of energy per electrode surface cannot be carried high.

The above-mentioned Gerard tube is cooled by means of oil, which is rather an unpleasant feature.

5. ABRAHAM-MARMIER.   Although it may be perfectly true that the Otto-Abraham-Marmier or rather the Abraham-Marmier ozonator does not contain any special ingenious feature
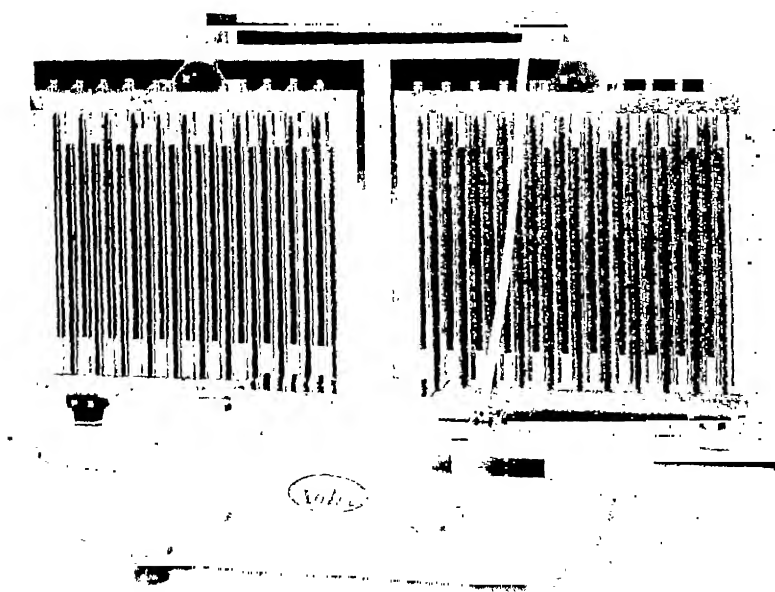

FIG. 44.—Small-Linder Ozonator (Vohr).

of its own, still it is also a fact that this apparatus is in actual use in several places in Europe, and on a pretty large scale.

Abraham and Marmier, realizing that a high-current density per unit area of dielectric means a high concentration of ozone, but at the same time also realizing that it cannot be done unless very efficient artificial cooling is resorted to, arranged matters in such a way that they had plane electrodes, but hollow, and have a current of cooling water run through them.

If both of the electrodes are to be cooled in this way, the cooling water would provide a short circuit, but this difficulty they have overcome by not feeding the cooling water tanks with a continuous stream of water, but by filling these by means of a drop system.

There are several ways of effecting a non-continuous flow of water, so there is no difficulty from that source.

Their ozonator gives ozone of very high concentration, and that is a necessity for the Otto system of utilizing the ozone in
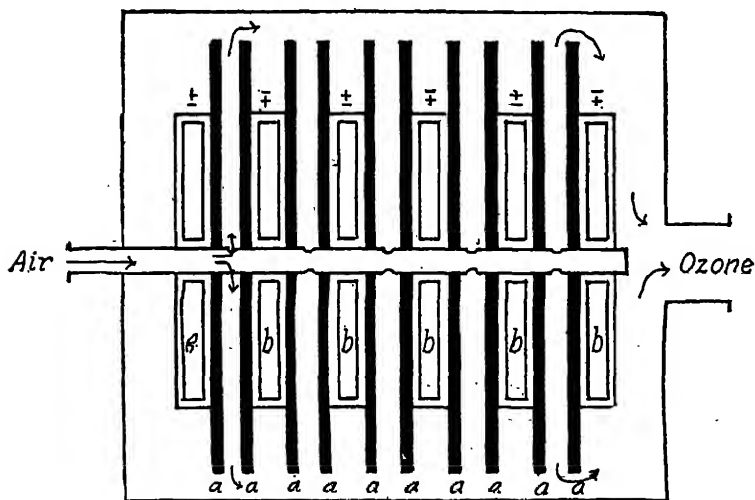

Fig. 45.—Abraham-Marmier-Otto Ozonator.

a special way, as we shall learn in the chapter on the application of ozone for the purification of water.

Quite a number of plants have been in operation for a considerable time now, and the Otto system as it is called has shown itself to be a great success.

The apparatus is shown in Fig. 45, the details are self-evident and need no further explanatory comment.

a, a, a, are the plate glass planes while b, b, b are the flat, hollow box electrodes, water cooled inside.

The usual tension for these ozonators is about 12,000 volts

CHAPTER XII

EFFICIENCY OF OZONATORS

6. VOSMAER. The failure of the Vosmaer non-dielectric system (the common fate of all non-dielectric systems) was an inducement to build a dielectric ozonator based upon the experience obtained with discharges. That much advantage was gained anyhow and viewed from a commercial standpoint it seemed of more importance to have an ozonator of cheap and simple make than to have one specially adapted for high concentration.

There are but few applications of ozone that require a highly concentrated ozone, but simplicity of design is of great value in order to insure reliability.

Our new ozonator is of the grid type, similar to the Small-Linder type, but differing from this in all details of construction.

In the first place the dischargers proper are constructed as follows: according to the nature of the brush discharge the electrodes are unlike in shape, one being a sharp knife-edge and the other flat, the first discharging from both edges.

The dielectric consists of a glass strip of special glass and is placed against the flat discharger, thus leaving the air space free for the stem of the brush.

The ozonator is composed of a number of these discharging units, according to capacity. Fig. 45 a gives a sketch of the same.

The strips $aaaa$ represent the sharp edged dischargers, b is the air space, c is the dielectric and d the flat counter pole. For reasons of cheapness in construction these flat counter electrodes may all be joined to a die casting.

High tension current (about 10,000 volts) is to be supplied to the sharp dischargers $aaaa$ by means of wires passing through the top of the apparatus and insulated therefrom.
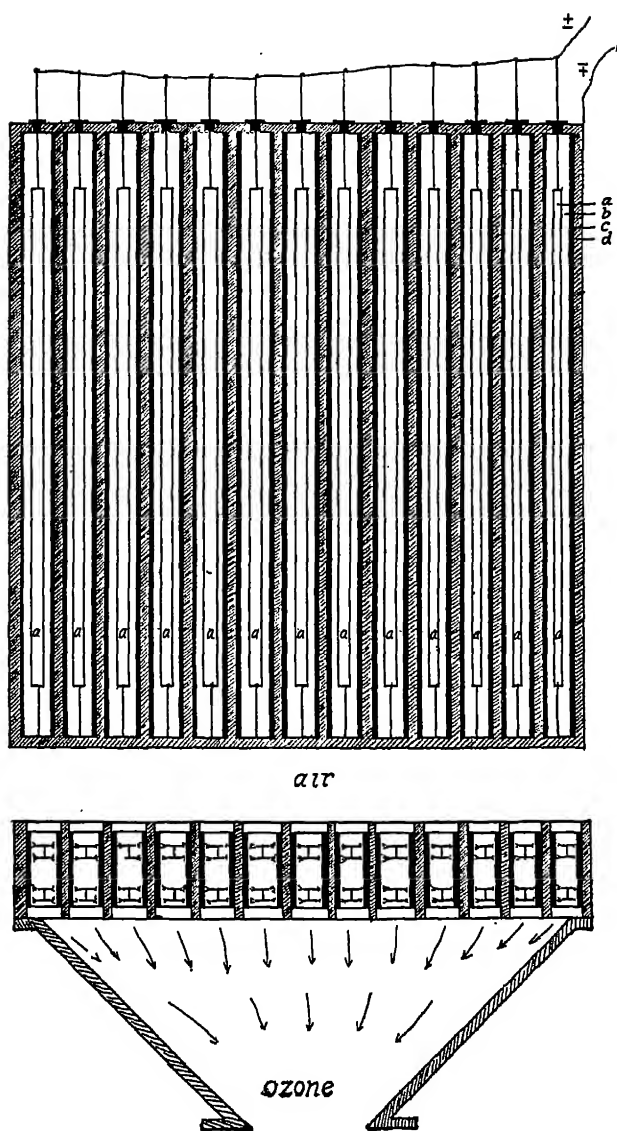
FIG. 45a.—Vosmaer Ozonator.

The placing of two pairs of dischargers in each compartment is a matter of consideration when large units have to be employed. The air coming in at the rear, in passing through the dischargers is ozonized, and the ozone is drawn out from the front, as indicated. The advantages of this ozonator are: cheap and simple construction, high efficiency, ample cooling surface when not overloaded, and reliability. The regular concentration of the ozone produced is about one gram per cubic meter. The regular yield is over 50 grams of ozone per kilowatt hour. Units are made from one hundred to one thousand watts.

Efficiency. It is customary to compare ozonators by their respective outputs in grams of ozone per kilowatt hour, but that is hardly fair to some of them because output and concentration are opposed to one another, and as one type is more especially adapted for a very high, and the other for a medium or a low concentration, different types are not comparable without comment.

The Gerard type is said to have a yield as high as 80 gm. at a concentration of about 3 gm. per cubic meter. These are rather high figures, but they do not mention for what length of time the apparatuses will give that much without interruption of work, and that point may be of far more importance than the question of output itself. The concentration can be much higher but not with the same 80 gm. of output.

The Vosmaer ozonator has a yield of over 50 grams at a concentration of one gram.

The Siemens tubes seem to yield about 50 gm. per kilowatt hour at a concentration of about 2.5 gm. per cubic meter and this is achieved without trouble.

In Fig. 46 we reproduce some curves for yield—in connection with quantity of air blown through, that is, yield to concentration —published by the Siemens firm and which are very interesting.

It should be remarked that the output is given in horse-power hours instead of the more logical kilowatt hour.

We do not see the advantage of expressing yield per coulomb ; we are used to speaking of ampere hours capacity of a storage battery, or to electrolytic deposits per ampere hour, but that is because it is understood that the tension is a constant which need not be repeated every time.

Here in the case of brush discharge it goes without saying that there is no bearing of output on voltage, but that does not

nean that this is a constant. It greatly depends on the type
of ozonator used, and one should rather express output in energy
dimensions, and not in capacity dimensions, leaving it to the reader
to guess at the other factor of the energy supplied.

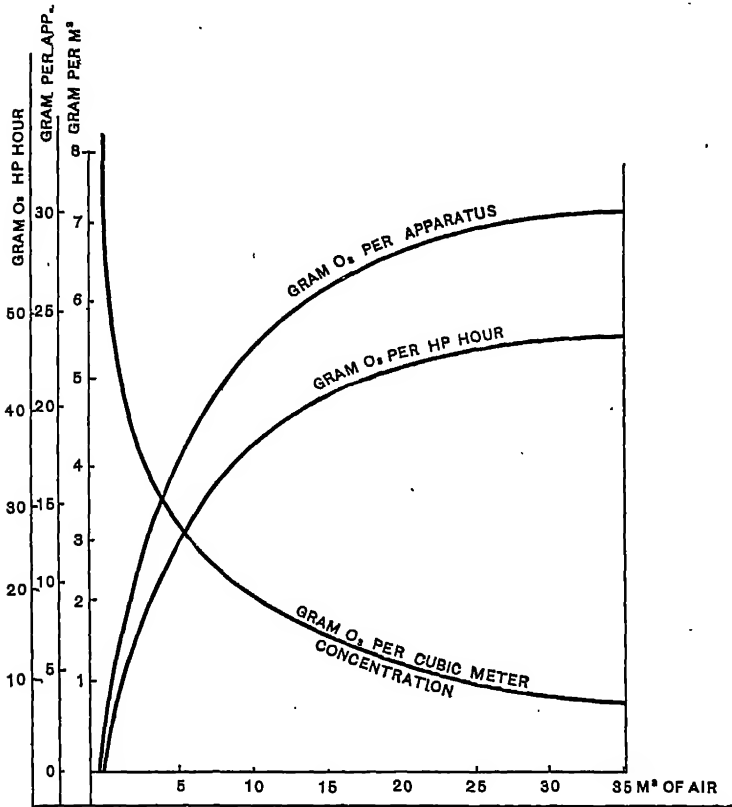Warburg[1] also says that the thickness of the dielectric has

FIG. 46.—Yield-concentration Curves.   After Siemens (Erlwein).

no effect, but that one dielectric instead of two gives a better
yield *because* there is less capacity.   This does not seem very
clear; one dielectric instead of two brings the electrodes nearer
together and thereby increases the capacity of the apparatus
considered as a condenser.

[1] E. T. Z., 1907, p. 629.

A change in the thickness of the dielectric materially affects the tension required to have the discharge, and in that way also affects the output per watt though perhaps not per ampere second.

From these and different other controversies, the reader will understand that there are several points yet that are to be settled; much would be gained if different workers could agree to work on a technical scale when dealing with technical problems.

Where Kabakjian[1] says that the yield in ozone is greatly increased by increase in air space, and hence in capacity, he should have added the words: " up to a certain point." He refers only to very small air spaces.
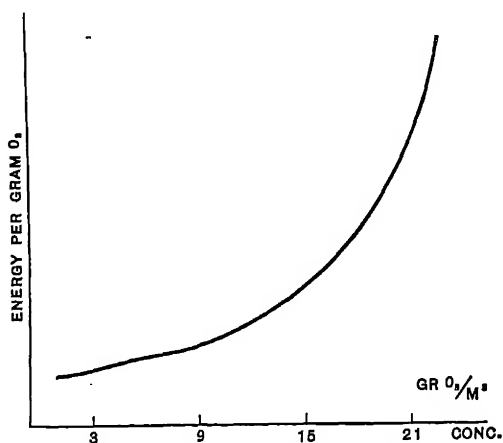

FIG. 46a.—Energy-concentration Curve.   After Chossi.

He says that increase in air space from 0.6 mm. to 3.2 mm. doubled the output and that is quite in accordance to what we might expect after a look at our photo of a brush, Fig. 6. As long as the straight stem remains straight, increase in polar distance will be beneficial, but beyond a certain value any increase will result in a lower yield, the maximum corresponding with about 3 to 3.5 mm. (the length of the stem again varies with polar distance).

Kabakjian[1] also adds that yield is an almost linear function of current and independent of voltage, except for the starting moment. His graphs, Fig. 47, show the bending point at a tension

1. Phys. Rev., 1910, V. 31, 117, 122.

of about 4000 volts; this value of course varies with different dielectrics and conditions.

Contrary to the (wrong) statements of Warburg, Kabakjian says that the yield per coulomb for different thicknesses of dielectric varies directly as the thickness, and consequently, in the inverse order of the capacity. See Fig. 47.

The increase in yield by decrease of capacity does not necessarily mean an increased efficiency, since the voltage necessary to give a certain current in the gas is much higher in the latter case.
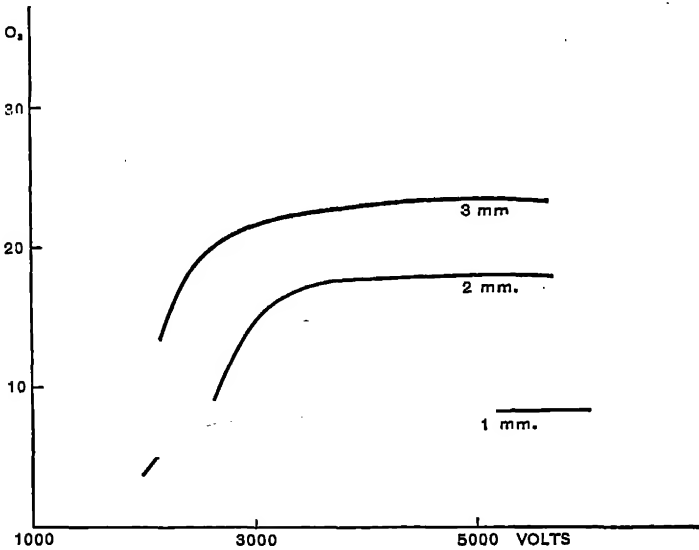

FIG. 47.—Yield-voltage Curves. After Kabakjian.

His conclusions are:

1. After a full steady discharge is established the quantity of ozone is almost in direct proportion to the current. The quantity is independent of voltage.

2. The yield of ozone greatly depends on the capacity of the apparatus; it increases with decrease of capacity, and the efficiency of the ozonizer increases with increase in capacity.

3. No definite voltage is required to generate ozone; it may be as low as 800 volts.

Evidently Kabakjian attaches much value to the capacity of the ozonator as regards its influence on the ozone output. Unfortunately the source quoted (Phys. Rev., 1910, 117 and 122) does not mention the relation between the effect on the ozonator and that on the circuit, but it may be seen from all these quotations that the information given by Kabakjian is of more value than that given by Warburg, when we think of commercial ozonators.

Among the many ampere-volt lines there is one given by Kabakjian which explains the characteristic behavior of ozonators using a dielectric. In Fig. 48 we reproduce a curve showing
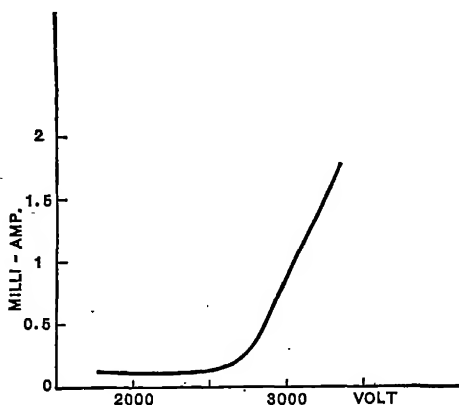

FIG. 48.—Volt-ampere Curve.

the influence of a mica dielectric of 0.05 mm. thickness. The electrodes were of tin-foil and the polar distance 1 mm.

In case of an ozonator having a large surface of discharge the density of charge per point or per single tiny little brush is low.

In our large 20,000-watt ozonator without dielectric we had about one and a half million points, the tension being about 10,000 volts; this means there was a current of 1.3 milliampere per single one, certainly not a large energy value, viz., 13 milliwatts.

In modern ozonators, using a dielectric, the current density is a large multiple of the figures given above, hence their higher efficiency.

It should be borne in mind that the ordinary calculations and considerations for sparking distances and critical voltages are greatly affected by these extremes, and that the brush discharge does not give much time for other discharges.

This value for the amount of current from a point is much in excess of that given by Precht as 10^{-7} ampere for a voltage of 8000, it being 1.2×10^{-6} for the same voltage.

As we shall see in the chapter on the uses of ozone, even at present its future is bright, so that would justify any amount of experimental research and expenditure of money and time to study the matter, but it will also be evident from that which has been mentioned that ozone is no subject matter for the layman and amateur experimenter.

The discredit ozone has fallen into surely is due to the fact that absolutely incompetent people considered themselves quite bright and shrewd enough to lay hands on this particular branch of scientific electrotechnics. The ignorance and conceit would be amusing, were it not that it does so much harm to the credit of the subject.

Although the action of the brush discharge on oxygen is of preponderating importance for the present, it may very well be that within a short time it may become evident that on other gases its action is of none the less importance.

Warburg[1] said that he obtained nitrogen-oxide when using spherical electrodes in air, and in fairly large quantity, but Warburg does not go in for technical apparatuses and sticks too much to the laboratory experiment.

There is one extremely valuable contribution on the action of the brush discharge on different substances, namely that of Collie.[2]

Collie says: " Mind that our laboratory pyrogenic methods are quite distinct from biological ones."

" Photo synthesis, the fundamental synthesis *par excellence*, which plants are enabled to accomplish, is as yet without a laboratory parallel."

" The chemist supplies energy in the form of heat, but by means of the brush discharge a mixture of CO or CO_2 and H_2 gives CHOH and CH_4 (Brodie, 1872), and Fisher has shown how sugars may be made synthetically from formaldehyde."

1. E. T. Z., 1907, p. 629.   2. Trans. Chem. Soc., London, 1912, II, 1540.

Thénard showed that H_2O is slowly decomposed by the brush and the slow combination of N and H is induced by it.

Berthelot noticed that many organic substances when submitted to the brush discharge gave acetylene, and later he proved that methane, ethane, ethylene yield a little acetylene plus some free hydrogen, and some resinous condensation products.

Losanitsch and Jovitchitsch confirmed the observation that CO and H_2 give formaldehyde. They also state that hydrocarbons polymerize under the influence of the brush discharge.

Collie himself found that carbonic acid is extremely unstable when at low pressure and exposed to the action of the brush, at a pressure of only 6 mm. upward of 65 per cent of the CO_2 being converted into CO and O_2 within ten seconds.

From all these observations it seems that the action of the brush discharge on various elements and compounds in many cases runs parallel with that of the action of light in plants:

H_2O and CO_2 decomposed to CO and O.

N and H combined to NH_3,

C and H combined to form $CHOH$,

and polymerization induced.

The following points are the most interesting:

Ethylene gas under the influence of the brush discharge at ordinary pressure and temperature not only unites with CO, but also polymerizes, yielding a series of complicated hydrocarbons, having the formula $C_{10}H_{20}$; moreover this molecule loses hydrogen and in turn yields a substance possessing properties somewhat like those of India rubber, and of a composition very near to $(C_5H_8)_{x}$.

In conclusion Collie says: the brush discharge seems eminently fitted for supplying energy to compounds; there is very little heat and consequently little chance for decomposition.

In recapitulation of Part II we may say that there are several methods of making ozone, the so-called chemical and the physical.

Among the first we mention the action of fluorine on water, that of sulphuric acid and permanganate of potassium, or certain metallic peroxides and that of slow oxidation of phosphorus; none is of any commercial importance.

Among the second the electrolytic method does not occupy

the position that it deserves, probably for lack of interest in the subject.

The other electrical method is that by which brush discharges are used to bring about the conversion of oxygen to ozone, and this method has been developed to such an extent that ozonators are now in the open market for various uses and of different makes for low and high concentration of ozone.

PART III

USES OF OZONE

CHAPTER XIII

PURIFICATION OF DRINKING WATER BY OZONE PROCESS

THE purification of drinking water has ceased to be a problem. The solution as found in the treatment with ozone is an accomplished fact, and the general application is only a matter of time—probably of a long time, because it is not the difficulty of the matter itself that has to be solved, but the ignorance and the prejudice of the public, and we shall see that this prejudice has its ground in the many failures of the past.

There are few men who know something about the ozone treatment of water, still less know the process from experience, but those who do know all agree on one point—namely, its efficacy.

The first results obtained by technical people and published, have been followed by numerous tests by scientific men outside of the business, and a great many scientific reports are at hand all agreeing that the effect of ozone on water is something marvelous and its superiority beyond question.

We must differentiate sharply between the action of ozone on water and the possibility of commercial application of it.

We shall discuss the first point briefly, because it can be nothing else than a repetition of what other scientists have said.

Although it may be that the use of ozone for the sterilization of water is much older, yet it must be acknowledged that not until Tindal in his plant in Holland, working with the Schneller patents, had shown the practicability of the process, was there any interest in the statement, made by Froelich in 1891, that ozone seemed to kill bacteria in water. Tindal worked in 1894.

The latter aroused the interest of scientific people in this subject, and practical men did not see any chance of application until the matter was brought before them in a simpler way and on a larger scale.

The evidence of success is to be had from a great many plants that have been in actual operation for a long time, and are not only still operating but increasing their capacity.

No smaller city than Paris has adopted the system of purification of water by ozone. After experimenting with it for several years, the city officials were not content just with a short trial, but wanted to have a plant run for more than a year before adopting it.

There is any amount of evidence to be had that in Europe the success is irrefutable and yet here in America people are not daring enough to even *try*.

The explanation is not far off, the application of ozone is of a very simple nature for those that know how to handle it, but it is no easy matter for those that have looked at it, and believe themselves clever enough to copy it.

It is from faulty engineering that so many failures have resulted.

Ozone does the work, that is a fact beyond question; ozone can be made in any quantity; that is another fact, but it does not include that every layman, "inventing" an ozonator will be able to manufacture ozone on a large scale and apply it on a commercial basis.

The application of ozone has been carried out satisfactorily in quite a number of places in Europe and so if failure results, it is not the ozone that is at fault but either the system or the management.

After the first publications about the wonderful action of ozone as a germicide, a question that very much interested the German Imperial Board of Health was: will ozone also kill pathogenic bacteria?

Experiments with cholera and typhus bacteria are rather awkward to be carried out in a private plant, handling say a million gallons per day, and the firm of Siemens & Halske were very fortunate to find the Prussian State officials willing and ready to test this matter.

In the proceedings of the said Imperial Board of Health,

1902, Dr. Ohlmueller and Dr. Prall published results of their investigations regarding the action of ozone on bacteria, and the selective action as regards pathogenic kinds.

The experimental series covered the effect of ozone on pure water infected with 16,000 cholera, or with 30,000 to 40,000 typhus, or 30,000 to 36,000 coli bacteria; the result was absolute sterility after treatment.

The next step was to see the result on infected ordinary river water carrying over 40,000 bacteria. After treatment some 5 or 6 were left over, and these were of an absolute harmless kind.

A year later Drs. Proskauer and Schudel of the Koch Institute, when having tested the ozone plants for the waterworks of Wiesbaden, concluded that ozone when applied in the right way was a reliable method of sterilizing water in large quantities (by the way, it may be remarked that this plant was erected by the firm of Siemens & Halske after their success in Martinikenfelde, and a third plant followed for Paderborn).

The many publications of Dr. Erlwein of this firm give full and trustworthy information about a great many details, and what we say about the Siemens installations has been taken from his publications.

Erlwein has published in different periodicals, at different times, and always in that sound manner that distinguishes scientific publications from commercial pamphlets.

As said before there are quite a number of reports on the effect of ozone on water and there is not one among them that is not in favor of it, and at the present moment we can say that we can know beforehand what will be the result of the ozone treatment.

It would be a long and monotonous tale, were we to excerpt the reports of Dr. Weyl on the Siemens system; those of the Profs. van Ermenghem, Roux, Calmette, Gerard, Ogier and others on the Tindal System; those of Dr. H. J. van 't Hoff, de Kinder, Dr. Rivas and others on the Vosmaer system, those of Roux and Calmette on the Abraham-Marmier system; those of Miquel and Daage on the present Tindal system in Paris (under the name of de Frise); those of Soper, Rideal, etc. It is all one tale of success as regards the *effect* of ozone on water.

Quite another question is that of the most economic applica-

tion, and on a large scale. There it is that some new unforeseen difficulties come in, and that is more interesting to learn because there is more variety.

One example is the trouble experienced with a type of sterilizing apparatus when quite unexpectedly the amount of iron in solution in the water turns out to be a good deal more than reckoned with.

We shall now consider some details of the application itself; as it is of the utmost importance to accomplish the reaction in a suitable apparatus.

When we say that ozone sterilizes water it is understood that some essential conditions are fulfilled. The ozone must be strong enough and above all must be allowed time to do its work. One cannot expect the action to be immediate because the contact of ozone and water cannot be molecular since ozone does not appreciably dissolve in the water.

The reaction between ozone and the organic matter in solution in the water is quite remarkable as we shall see presently, and its action on bacteriological life is most wonderful, but the factor time plays an important rôle in the accomplishment. It is rather curious to note how many people, working on ozone, do not or did not realize the absolute necessity of prolonged contact.

Let us first consider the action of ozone on the organic matter in solution in the water. Unfortunately we chemists do not know what they are, and it is customary to join the whole lot together under the name of organic matter, and to express the quantity by the amount of permanganate of potassium it takes to oxidize it in acid solution, conforming to a certain standard method.

Some people prefer to express the amount in a figure for oxygen; 1 mg. permanganate (per liter water) is equivalent to ±0.25 mg. of oxygen ($2KMnO_4 = 5O$). We have not the slightest idea as to what kinds of organic compounds there may be present in different waters, but it is a fact that ozone exerts an oxidizing action, though strange to say it never oxidizes all of it, as a rule no more than about one-half, maybe 60 or even 70 per cent, but that is not the regular work; it goes to higher percentage in bad water than it does in good water, and we are not far wrong when we say that it is the amount of organic matter

that determines the amount of ozone to be used in sterilizing water.

The amount of bacteria does not matter at all; it is quite the same as to results whether there are a thousand or a million of these, provided the sterilizing apparatus be such as not to allow the smallest particle of water to escape the action of the ozone.

This is easy to understand. Suppose one-thousandth part of the water escapes the action of the ozone; then if there are less than a thousand bacteria, the chance is that a sample will be found void of bacteria, but if there are a million, then if one-thousandth part is not sterilized there will be a thousand left!

If it is possible with a certain apparatus to sterilize a water containing a very high number of bacteria per cubic centimeter, that speaks not for the ozone but for the apparatus in which the treatment is carried out. We shall come back to this point.

To have a chemical reaction brought to a finish as a rule there is a certain amount of time needed. True there are reactions called explosions which do not require much time to finish, but these are of a different class.

Now in this case of ozone treatment we are working under rather unfavorable conditions in so far as the temperature is never much above that of the surrounding atmosphere. By the way it may be said here that the author never found any difference in working either in winter or in summer time (Holland).

The next unfavorable circumstance is that ozone has to do its work on the *surface* of the water molecules; as it is not appreciably soluble, we are having a case of what we are used to call mechanical contact, not mutual molecular contact.

It is true that it is oxygen in its atomic or nascent state, that is acting on the organic matter, but this itself will not be in such a state.

Chemical reactions between substances in solution and non-soluble gases are rare and not very prominent; here in case of ozone it must surprise the chemist to learn that the oxidation of organic matter in solution is carried out by ozone with ease when there is time given in addition.

(The chemical method for analysis of organic matter is carried out by permanganate in a boiling acid solution for ten minutes.)

In order to fully appreciate the strong action of ozone it may

be said here that ordinary oxygen gas bubbling through water at ordinary temperature has very little or no effect on the organic matter (of ordinary water).

The next point to consider in water in regard to its purification by ozone is its iron content.

Iron can be present in waters either in the ferrous or in the ferric state; the first is very easily gotten rid of by aeration, but the second is a difficult problem to solve unless we have ozone, the ozone taking care of organic ferric compounds, oxidizing these to ferric hydroxides, which of course have to be removed from the water by some process of filtration or centrifugation.

The ordinary contents of water: nitrates, nitrites, ammonia, albuminoid ammonia, etc., are of no importance in themselves; and their determination has no other object than to be a guide as to the probable degree of contamination, and from what source it comes.

The ozone treatment does alter these amounts to a certain extent, but there is no reason for satisfaction over that, because nobody really cares for it, if the water contains no harmful bacteria.

The mineral contents are not changed by the ozone treatment to any appreciable degree; there may be cases in which some change actually does occur on account of secondary reactions, i.e., ozone drives out the carbonic acid, and that may be a cause for change in mineral contents.

A very prominent change occurs in the content of free oxygen, the water after due treatment will leave the apparatus nearly saturated with oxygen, which is very beneficial to its taste.

The oxygen does not come from the ozone, that would indicate a splitting up of the O three into O two and one atom of O, in which we do not believe.

The excess of oxygen in the water is simply due to the fact that the ozone as it is applied, is diluted with air and the bubbling through of this causes oxygen to be taken up.

In the amount of ozone consumed when organic matter is oxidized is another proof of the statement, that from ozone there are three atoms of O available for oxidation.

The amount of ozone required to purify the water depends entirely on its content of organic matter in solution and corresponds very closely to the amount of permanganate oxygen.

For example, if we have to sterilize a water titrating, say, 10 mg. of potassium permanganate, that means about 2.5 mg. of O, it will require about 1 mg. of ozone, O_3, not three times as much, to do the work. We have already said that as a rule only part of the organic matter will be oxidized, generally less than 50 per cent, sometimes only 35 per cent, sometimes over 60 per cent.

As 2 molecules $KMnO_4$ yield 5O or 316 give 80, it is clear that when we have O_3, it must yield all three of its atoms; only then will it be able to do the work as indicated above.

Should ozone yield only one atom, then, as the other molecule of oxygen does not act upon the organic matter, we would have to have three times as much of it. This, to the author, seems a conclusive practical test of the theoretical probability discussed in the first chapter that ozone is not a molecule of oxygen with a third atom just hooked on, but a definite molecule of O_3 splitting up into three atoms of O.

So much for the chemical side of the treatment, to which may be added that when a bad taste has its origin in certain organic matter the improvement with respect to this taste comes from the chemical action on the organic matter, and if we investigate, the improvement in color and smell are also due to chemical action.

In fact, ozone takes out between 40 and 60 per cent of organic matter in solution; furthermore, it takes out iron in solution, no matter whether in the ferrous or in the ferric state; then it takes out any discoloration, any odor and all bad tastes, thus rendering the water fresh and pleasant.

Ozone owes it fame to its remarkable power of killing bacteria when these are present in water; that is why all the world should look upon ozone as a boon for mankind, since we all know that pure drinking water has very much to do with health, or it is perhaps more correct to say, since impure water is responsible for many a disease, more especially typhoid and cholera.

This latter is not of much importance in every-day life; cholera epidemics are rare in civilized countries, but typhoid is quite common, and in America the death rate is many times what it is in Europe on this account. Considering that only about 10 per cent of the typhoid victims die and realizing that there are 90 per cent of whom we do not hear, but who have also been suffering

and fearing unnecessarily, we might expect more interest taken in this country in a system of water purification that is efficient and cheap, one that has stood the endurance test in several places in Europe, and is in fact, making fairly rapid progress there.

In his report on national vitality, Prof. Irving Fisher repeatedly points out the importance of a pure water supply, and also lays stress on the money value of health.

Is it not rather a strange fact that several methods for the purification of water have been tested and are in actual use, and that the ozone method, which is a complete success in Europe, is neglected here?

We shall discuss the relative values of different methods for the purification of water presently.

Bacteria are plant life of about the lowest type; their power is in their multitude, and their multitude is due to the rapid multiplication by striction, called segmentation. There are numerous kinds, some of which are very resistant, others very little resistant; fortunately those that are harmful are among the least resistant.

Some kinds of water bacteria are very resistant and form spores, but those are absolutely harmless. There are no pathogenic spore-forming bacteria in water.

Neither the cholera nor the typhoid bacterium belong to water. They may occasionally find their way there and stay some time, but they cannot live a long time in water of ordinary temperature. That is one of the reasons why after all such a simple method of purification as storage has its good sides, provided the time of storage is over a fortnight, or three weeks, which, by the way, is a long time and means a tank or basin of enormous capacity, if we have in mind the water supply of a large city.

We must not take chances when considering a central water supply, and must bear in mind the diseases.

Of the numerous water bacteria there are but few of interest to us; they are the B. ramosus, the B. mesentericus, and the B. subtilis, which latter one is not subtle at all, in so far as though it is very small it is a very resistant one, but perfectly harmless.

These three kinds may and in most cases do survive the ozone treatment; anyhow a few of them do, but that does not

trouble anybody. It is quite féasible to render the water perfectly sterile, but at the expense of more ozone and a stronger ozone or longer treatment. As we are considering the ozone treatment from a commercial standpoint it would be rather a waste of money to have the process pushed so far as to obtain perfect sterility, as it would be nothing but waste of money to free water of a few harmless bacteria. What we are after is the killing of typhoid and cholera germs, and incidentally also the *B. coli*, not because all the coli are harmful—on the contrary we would soon die from constipation had we no coli—but for practical reasons.

If there are no coli in the ozonized water we can be sure that there are no typhoid germs either. There is very much similarity between these two, but the coli are much less sensitive to ozone than are the typhoid, so the absence of the former serves as an indicator that the latter will be absent also.

The testing for typhoid bacteria, of which there are many kinds, is not such an easy matter, and it is very convenient to have an every-day simple check method. There are scientific institutions that have done remarkable work for us when testing the power of ozone in the matter of specific action on pathogenic kinds. This is very delicate work, not easily carried out in an ordinary laboratory, but this point being settled without the least controversy it is easy for us regular day workers to check the action of ozone in a quantitative manner, in so far as it evidently is quite sufficient to control the number of bacteria.

The actual number of bacteria present in a water is of no importance at all as far as the action of ozone is concerned; it makes no difference whatever if there are a thousand or a million of them—as said before the quantity of ozone required to do the work satisfactorily depends solely on the amount of organic matter in solution and has no bearing whatever on the actual number of bacteria.

But these two factors are not independent in so far as that a very large number of bacteria cannot be present in water that is very low in organic matter.

The only way in which the number of bacteria influences the result is in the accidental escape of a small droplet which tells more when that droplet contains a large than when it contains a small number of bacteria, but this at the same time is an excellent test for the efficiency of the sterilizing apparatus.

If this is a good one we do not care about number; if it is a faulty arrangement, say a spray in a chamber containing ozone, then the defect becomes evident.

It may seem incredible to those who are familiar with bacteriological life, but it is true nevertheless, that there are a great many people that feel uneasy about the *carcasses* of those killed bacteria.

The public in general neither realizes the extreme smallness of the bacteria nor the fact that they are plants, and that we need not take notice of the remains. The question has been asked a good many times, and that is why we may just call attention to the desirability to calculate this matter in figures.

Let us take an extreme case, say there are a million bacteria in a cubic centimeter, (the actual amount seldom exceeds ten thousands) then if we think of a cubic meter we are having 1,000,000,000,000 in all.

Let us further take the size of one bacterium to be about 0.001 mm. in diameter, that means that the volume is 0.000000001 c.mm.

The total size of all of them together will thus be 1000 c.mm.

Now a bacterium contains about 90 per cent water [1] and of the remaining 10 per cent of vegetable matter there is no more than about 0.1 of mineral matter, and so our volume of 1000 c.mm. contains 1 c.mm. of mineral matter, called carcasses by the public.

Now that 1 c.mm., about the size of a period in print, is all that is left of that tremendous number of bacteria in 1 c.m. but not only is it so very little, but what do we care for a little vegetable ashes.

The mistake is that the average man does not and cannot realize the smallness of the individual being, and thinks too much of animals swimming in the water and certainly they think so if they happen to have had the good fortune of seeing moving bacteria under a microscope. There are a great many people who feel some fright when being shown pathogenic bacteria under a microscope and who feel uneasy when being at the same time told about their peculiarities.

The fact that there are spore-forming bacteria not attacked by ozone leads to the supposition that the action of ozone is

1. Some people say 85 per cent.

rather more a specific killing than a simple burning up.   It seems probable that both actions take place.

There are people who believe that ozone kills through coagulation of the albumin.   This is not very probable as we have bleached eggwhite with ozone and experienced no trouble from coagulation, and in that case we had animal matter, which is far easier to coagulate than vegetable albumin.   It is to be hoped and expected that as soon as the sterilization of water by ozone will have become a common thing the interest in the theoretical side will also be aroused.   Much more light is needed in this very special branch of applied science.

On more than one occasion have we spoken of sterilization and that word has had its meaning extended a little in the water business.   We may here speak of a degree of sterilization; of course we all know that is wrong; sterility does not allow of a gradual comparison.   Something is sterile or it is not so, and sterilization should be complete, for when it is not it is no sterilization, but here, as in many similar instances of applied science, a word is used for convenience' sake in a broader sense than is strictly correct.

We only want to call attention to the fact that we are aware of the mistake but are yielding to the common practice of considering or rather calling, the purification of water in regard to its bacteria content *sterilization*.

We have already mentioned that the effect of temperature on the action of ozone does not seem to be noticeable within the common range of winter and summer, though probably a higher temperature will favor the action of destruction.

The action of ozone on gases in solution is nothing particular; of course, carbonic acid when present is driven out by the excess of ozonized air blown into the water; this is according to the rules of physical chemistry, and so is the fact that the water after having been treated with ozonized air will carry a great amount of oxygen, sometimes up to its saturation point.

EFFECT.   If we now summarize the effect of ozone on water we have the following points:

CHEMICAL.   Ozone oxidizes organic matter in solution, not all of it, seldom more than 70 per cent, usually more than 40 per cent; the percentage removed depends also on the original amount present, it being the higher the higher this was.

Ozone influences the amounts of nitrites, nitrates and ammonia, but its effect is of little importance.

Ozone has no influence on the mineral compounds, except in so far as it influences the free carbonic acid, but none of these have any importance when we treat water with ozone, the very complicated water analysis except a few determinations can be omitted.

The effect of ozone on iron in solution is two-fold; the ferrous compounds are all turned to insoluble ferric compounds, and the ferric compounds are decomposed so as to form non-soluble products, as iron hydroxides.

PHYSICAL. Any discoloration of the water is removed by the ozone treatment, as are bad taste, odor and opalescence.

Turbidity, caused by matter in suspension, cannot be altered by ozone. After all, its action is chiefly chemical, and thus turbidity, being caused by mineral matter, say clay or sand or such like, will not undergo any change. The excess of air will cause all other gases to be expelled, except for traces and the result will be saturation with air, the advantage of which is a saturation with oxygen.

For purely practical reasons it is desirable that there should be used a slight excess of ozone, so as to be sure there has not been too little of it.

This excess, too slight to affect the cost of the process, will be an indication of good work, but as ozone is soluble in water to a very slight amount only, and certainly will act very powerfully in that state on the matter in solution left over, any excess is got rid of within a very short time. The water running out of the sterilizing apparatus has a strong smell of ozone, but ten or twenty seconds are quite enough to have it disappear entirely from the water.

BACTERIOLOGICAL. Ozone destroys bacteriological life in water. No matter how many bacteria there may be, ozone will take care of them and destroy any amount and any kind. For practical reasons, however, it is desirable not to push the treatment to the extreme when in regular, everyday work, so as not to increase the cost without any further benefit.

The bacteria which are left behind when ozonization is carried out in the practical way are invariably of the absolutely harmless kinds.

When so desired, the ozonization can be carried on until complete sterilization is obtained, but that would be useless, except in certain special cases.

The remains of bacteria are not worth while considering; they are far beyond our ordinary means of observation.

The action of ozone is selective in so far as the pathogenic bacteria, which are less resistant, are oxidized first.

It is more or less disputable whether the action as a germicide is to be considered as a chemical or as a physical one.

Suppose we distinguish chemistry from physics as being more quantitative, while physics is more qualitative, then in the case of ozone we feel its action to be rather physical in character, realizing that for the sterilization of a water very low in organic matter, one in 10,000,000 parts is sufficient to do the work. Such a relation is in the order of physical phenomena, not of chemical reactions.

Even in ordinary water, carrying, say, organic matter equivalent to about 10 mg. of permanganate, no more than 1 gm. of ozone per 1,000,000 gm. of water is required; this circumstance is one that leads to the conception of considering the germicidal power of ozone as a specific and physical property.

The particular beauty of ozone as a means of purification of drinking water lies not only in its direct action of unsurpassed quality, but also in its secondary action—the after effects.

It is not only that the harmful and troublesome properties have been taken away through ozonization, but additional good qualities have been imparted; namely, the gain in freshness of taste, due to the excess of dissolved oxygen, and better keeping qualities for the same reason.

ENGINEERING. Ozone is the ideal method of purification of drinking water; nothing is left to be desired, not even the cost, and we shall see presently that even this is better than one would expect it to be.

As in all engineering undertakings, the cost of installation of an ozone water plant depends largely on its size, upon local conditions, and on the engineering skill possessed by the man who undertakes the project.

We are not supposed to discuss these engineering questions in detail, but some salient points may be considered in brief.

For a small plant it will, as a rule, be simpler and more eco-

nomical to buy current than to make it on the premises, but for a larger one, it would, of course, be the reverse. At what size equipment the balance of these two changes over, cannot be said; that again depends on many factors, such as price of current and locality. The current to be generated or obtained in some other way should be alternating and preferably of 500 periods. Many of the installations abroad are using this periodicity, and it seems that alternators for this high-frequency can be bought ready made.

This alternating current has to be raised in voltage so as to have at least something like 10,000 volts, or so much more when the type of ozonator used requires a higher voltage. A transformer will do this work.

The air which is to be ozonized had better be dried before entering the ozonator. This can be done in tanks containing burnt lime, or chloride of calcium, or by means of refrigeration.

It is needless to pay so much attention to the alternator, anything will do as long as it is of a modern type; details about wave form are of no practical importance. By way of illustration how some people may find details of " importance," it may be said here that in one of the many reports on ozone plants there is particular attention drawn to the fact that the current supply was a " brush " alternator. The reporter, evidently not so very well posted on dynamos, thought that the well-known English Brush alternators had something to do with the brush discharge!

The English Brush Company made dynamos long before anybody was thinking of making ozone and brush discharges.

Fortunately, the special kind of primary current matters little, when it comes to considering the amount of water treated by one unit of electrical energy.

We should not pay too much attention to details of that kind; so we take it for granted that alternating current of either the ordinary or of a high periodicity is supplying the primary energy. It is immaterial again what tension there is at hand; any regular tension will do.

The next point is the step-up transformer that has to supply the secondary high-tension current; this tension has to be about 8000 to 10,000 volts or so, as the particular make of ozonator requires; that again is of no special importance, but

one should be able to regulate the secondary tension to a nicety to suit the ozonator in question.

The use of additional electrical apparatus, to check phase-shifting, cannot be discussed here in a general way; that is for the designer of the installation to make sure that the whole, as such, is as economical as possible; that means that everything is in perfect harmony.

For the ozonator itself, there is choice enough between those that are placed on the market for different purposes. They should always be run in parallel. In all the larger installations abroad, ozonators are grouped in sets so as to give more elasticity to the system.

It makes no difference whatever whether one terminal of the high-tension apparatuses is grounded or not, that is a matter of personal preference in regard to safety, our personal practice is to ground one side.

The mechanical arrangement is none the less important for economic working; we have to handle large volumes of air as well as large quantities of water.

The air to be ozonized is generally subjected to a process of drying. This can be done in several ways—chemically or physically.

Drying by burnt lime is efficient but unpleasant on account of the mixing with dust of lime. Drying with chloride of calcium has become more popular since it has been carried out on a large scale for the drying of air for blast furnaces. We have been using chloride of calcium with perfect satisfaction for the purpose, the only secret about its success being the necessity of a large surface, in order to have the air pass over it slowly; not a high, narrow tower, but a broad, low one.

We must bear in mind that drying the relatively very dry air in America is much less costly than drying air in Holland, which is nearly always saturated with moisture.

In Holland the moisture seldom gets below 80 per cent and generally is about 90 per cent, in summer as well as in winter, but that only means that there are more grams of water to be absorbed by the chloride of calcium or a more frequent renewal of the mass; the degree of dryness can be the same in both cases, and is only a matter of vapor pressure of the chloride of lime solution at a given temperature.

This brings out an important detail, that of keeping the dryer cool. Paint it white and do not allow the solution at the bottom to be hydrated too much.

Another method of drying is that by refrigeration; it is less costly when large quantities are being handled, because its cost is partially recovered through increased output of ozone from the refrigerated air.

The efficient drying of air for ozone making is no difficult problem at all, and the cost of drying plays no important part in the total cost of manufacture.

Next comes the forcing of the air through ozonator and sterilizing apparatus. The great importance of this latter apparatus justifies a discussion at length. Let us first consider the ozone pump.

It seems to be the general practice to employ a suction compression pump for this purpose, the pump sucking the dried air through the ozone apparatus and forcing the ozonized air through the sterilizing apparatus.

This brings in a difficulty in the pump itself, in so far as the ozone causes trouble, no lubricant can be used, neither oil, glycerine nor graphite.

After some trouble we found an excellent solution for the difficulty, namely, to make ordinary piston rings, similar to cast-iron ones, but out of celluloid.

The celluloid is to be cut out of a plate as a strip, and bent in hot water to a ring, open, and with beveled ends just like a cast-iron ring.

When bent and put in position, turn the ring in the lathe.

An ordinary cast-iron piston running in a cast-iron cylinder and fitted with some of these celluloid rings will do its work faultlessly, without any lubrication, and there is, moreover, no great wear.

It is only a trifling difficulty, but one that has caused a great deal of trouble, and as our own experience in this line has been very satisfactory with the use of these celluloid rings, it may help other people out of the trouble. It cost us some time and money before we struck the idea of applying celluloid for this purpose. The secret is told in a few seconds, but not so easily found out.

There is nothing to be said about water pumps; that is nothing

but ordinary engineering practice. Most people seem to have used centrifugal pumps for this purpose, and so have we. Now we come to that most important part of the work, the sterilizing apparatus.

Sterilizers. There are different kinds of these and unless radically wrong, all do the work. Their difference is in their economy.

It is not only the question of sterilizing the water, but also of doing so for the least cost, or in this case, with the least amount of ozone, and that is where the relative merits come in.

In the chemical industry the problem of treating liquids with gases is a common practice. There are quite a number of processes whereby either absorption or action is sought, and unfortunately the same familiar apparatus for absorption; the well-known scrubber, has also been applied in the ozone business.

This was a mistake, as in the case of ozone and water we do not have a case of absorption at all—it is one of mechanical contact. The scrubber, see Fig. 49, is principally a tower filled with something like coke, pumice-stone, gravel, flint, or any other suitable material so as to offer a very large surface over which the liquid—in this case the water—flows in thin layers.
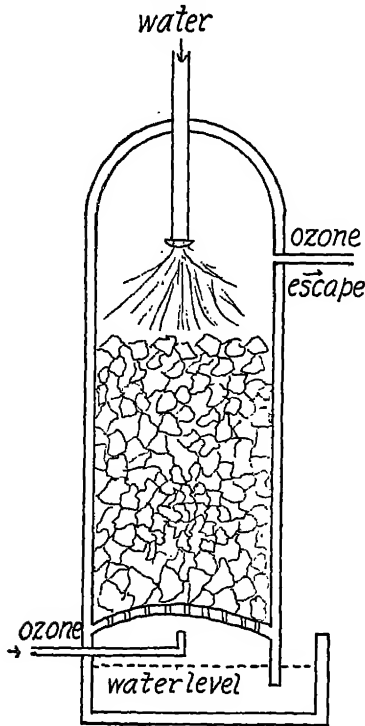
Fig. 49.—Siemens-Halske Sterilizer (scrubber).

The gas can be introduced at the bottom and so we can have the application of the well-known principle of counter current of the two ingredients. The downward flow of the water spread out over a large surface area, and the upward movement of the ozone finding its way through the hindrances.

This description seems all right but one should bear in mind that in the first place a very thin layer of water on the surface of a piece of flint is very thick in comparison with the dimensions of the bacteria, the things we are after in this case. Action cannot be expected to be complete unless the ozone present be of a very high concentration in order to penetrate the film of water.

We cannot regulate the time of contact between ozone and water because the downfall of water is beyond control in this apparatus, neither can we regulate the speed of the upward travel of the ozone, and the only way to make up for these defects is to make use of very strong ozone, say 2 or 2.5 or more gm. per cubic meter.

In actual practice only a fraction of that strong ozone is used up, and so as not to lose this costly ingredient, it is recovered at the top of the scrubber and used again, that is, it is to be passed through the ozonator instead of air and be regenerated to its former high concentration.[1]

This recovered ozone, however, is saturated with moisture and its complete drying is more costly and troublesome than the drying of outdoor air. Another mistake about the use of a scrubber for the purpose in question is that in case we deal with water high in iron content, the ferric hydroxide will cling to the surface of the obstructions and clog the passages. It is known that considerable trouble was experienced from this source in the first European plants.

The trouble has been removed by adding a device for removing the iron before ozonization.

The scrubber is essentially an apparatus for absorption and not for a contact so intimate as is needed in the special case of the removal of bacterial life in water.

The fact that in the scrubber the strong ozone demanded for the accomplishment of sterilization does not find opportunity to show its full advantage, and that the escaping gas has to be recovered, proves that the scrubber is not an efficient apparatus in this case.

The scrubber has been in use in the older Siemens plants. The high output in ozone of the Siemens ozonator was lost by the low efficiency of the sterilizing apparatus.

1. One has to replenish oxygen consumed in this closed cycle.

Tindal used quite a different device. In the original plant, see Fig. 50, he used a standpipe divided into compartments by perforated screens of metal. Here we can have no counter-current, water and ozone passing along for some time the same way. Tindal's plant has attracted quite a number of scientific people. The qualitative effect was very satisfactory, but the quantitative result was poor.

It needs no argument to emphasize the fact that counter-current is always the most efficient way of having substances act on one another.

The desire to have counter-current and experiencing the impossibility of having such in Tindal's standpipe, led us in 1900 to some boldness in this matter.

Let it be known first that it has been our habit to carry out experiments in glass apparatuses whenever it was possible to do so, because that enables one to watch closely what is going on and to see what changes when conditions are being altered.

We had the Tindal sterilizer made of glass cylinders, 1 ft. in diameter and $1\frac{1}{2}$ in length, placed one on top of the other, and the perforated plates between them.

It struck us that the mixing of ozone and water was good in the greater part of the cylinders but just below each compartment there was a layer of ozone (see Fig. 50), the downward flowing water leaking through and the upward movement of the ozone being temporarily checked by the water.

The fact is that water and ozone cannot pass simultaneously through a small hole, so they do it alternatively.

We had the perforated plates made out of celluloid and having made the perforations ourselves could easily change these, that is to say we could easily replace diaphragms with holes of say 1 mm. by another set with holes of $\frac{1}{2}$ or $\frac{1}{4}$ mm. in diameter; we also tried different shapes of holes, oblong, square, slits, etc.

The apparatus being made of glass it was interesting to watch the difference occasioned by different perforations; they were slight, and so we found that no matter what shape or size the perforation was ozone and water will not pass through at the same time unless the dimensions of the perforations are such that we cannot longer speak of them as small holes.

The thorough mixture of ozone and water was separated into its components at every perforated screen, and it was but a

water outlet

ozone

ozone

ozone

raw water inlet

ozone inlet

← water
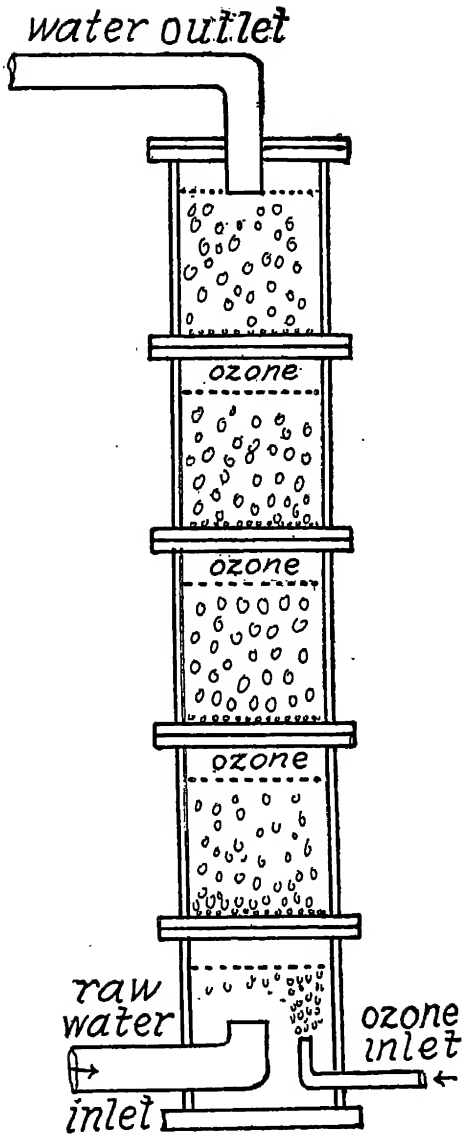
FIG. 50.—Tindal (de Frise) Sterilizer.

water inlet
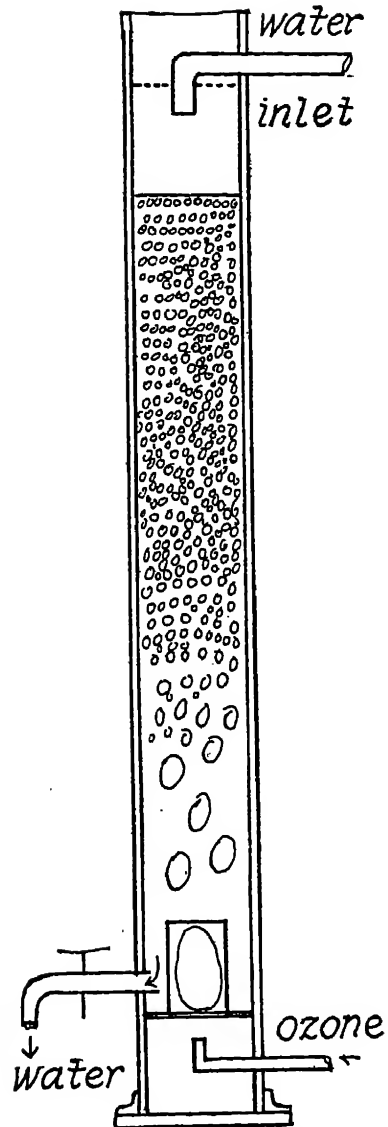
ozone

FIG. 51.—Vosmaer Sterilizer.

moment's thought to try the effect of no screens at all between the different compartments. The effect was marvelous. Instead of a column made up of partly mixed and partly separated ozone and water there was now one continuous mixture, like Fig. 51.

In view of what has just been said it is very clear, of course, that there is no separation. We have here a very interesting case of surface tension of a liquid, namely, the case of inside tension.

The bubbles of air in a mass of water will not unite into one, on the contrary, one very large bubble will split up into as many small ones as is dictated by the laws of surface tension.

A vertical jet of water is known to split up into single drops on account of surface tension. A purely physical reasoning shows that in small drops the ratio of surface to capacity is one that harmonizes with other circumstances. Now in our case we have the same phenomenon but reversed; there is not a splitting up of descending drops of liquid but of ascending gas in bubbles in such a way that the size of the bubbles corresponds to the conditions. The inside surface tension of the water is far too great to allow of one big bubble, and one of the most striking and instructive experiments was to start the gas inlet in the standpipe suddenly so that at the very first moment one big bubble, say 1 cu.ft. in size enters and it is only a matter of seconds to have this completely split up into small bubbles, about a quarter of an inch each (see Fig. 51). At a height of say 1 meter there is nothing else but a complete homogeneous mixture of gas and liquid, provided there be enough of the gas in question.

Thinking once more of the original Tindal type (now owned by de Frise) one would ask what is the meaning of those perforated plates between partitions, what is their rôle? The answer will always be, to have the ozone in very small bubbles. That is a mistake, however; the gas takes care of that itself out of its inherent properties, and the only action of the perforated plates is to destroy the auto division temporarily by having the gas accumulate under the screen. If our original Tindal sterilizing tower had not been made out of glass, we probably would not have known so soon that the perforated screens not only did no good but actually did much harm.

The only secret about the absolute success of this very simple sterilizing standpipe of ours lies in the true harmony between the different items, as there are: quality of the water to be treated,

its quantity, the diameter of the standpipe, its height, and the relative amount of ozonized air blown through.

Before all there should be such a large volume of gas that the whole section of the sterilizer is completely filled with a mass of water and gas. In this way we can have the liquid in nothing but surface films outside of the ozone bubbles and in that way sterilization is effected without much trouble.

The effect is startling at first, but one soon gets used to the fact that such a small amount of ozone as is present in a cubic meter of air when the concentration is but 1 gm. is capable of sterilizing water of ordinary quality as regards contents of organic matter in solution.

For no water and no amount of bacteria did we require more than a concentration of 1 gm. per cubic meter of air. If the water is worse than the average, more ozone is required to do the work but not of a higher concentration.

The fact that at the top of the standpipe the air comes out practically free of ozone proves that all that has been given has been used up. There is no need for any recovery since there is no waste except an insignificant amount, which is desirable, because it is an easy way of controlling efficient work when we allow a small excess of ozone.

As long as there is some ozone in excess, we can be sure that the process of purification has been carried out effectively.

Rather than recover the waste, we use all of the ozone introduced into the water.

It tells very much against the efficiency of an apparatus if one is obliged to recover the waste; the 99.99 per cent efficiency of our standpipe is due to its rational working.

The simple sterilizing apparatus just described does not appeal to anyone unless it has been seen in operation and tested for its efficiency. As a rule the more complicated apparatus makes more impression at first sight; ours is too simple, but it does the work better than any other arrangement, the word better meaning here: more economically.

In Fig. 52, the principle of the sterilizer is given in sketch. The water runs in at the top and is allowed to run out at the bottom, its velocity being checked by the valve 2.

The ozone enters the bottom at 3, passes through a perforated screen 5, and the air escapes at 4.

The screen 5 permits the ozone to pass through and pre-
vents the water from doing so; at 6 there is another screen, the
purpose of which is to allow
the water to pass through
and prevent the ozone from
doing so. This opposite
action of a similar screen
is based on the fact that
water and ozone cannot
pass simultaneously through
a screen. Now at 5 there
is more pressure of ozone
than there is of water so
the ozone prevails and goes
through; at 6 on the other
hand there is more pressure
of water than ozone and
thus the former prevails.
It is very amusing watch-
ing the action; occasionally
a bubble of ozone will be
led astray and try to es-
cape but it cannot, and
will therefore continue its
upward motion.
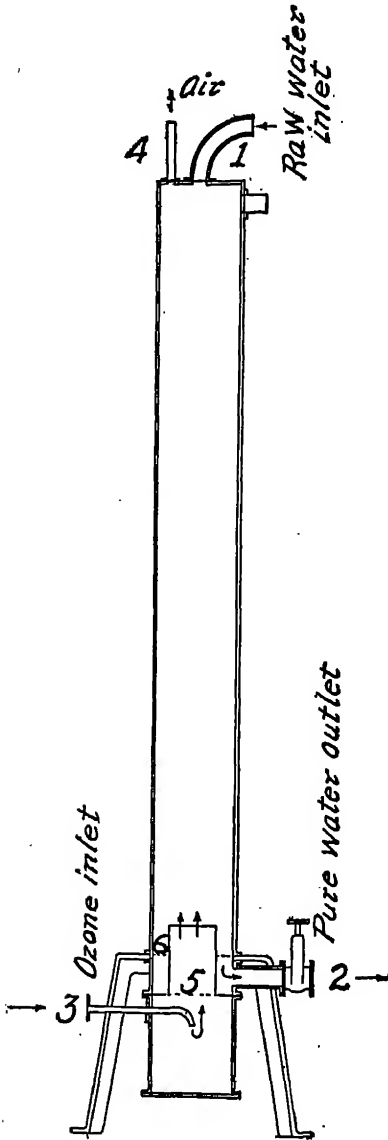
The peculiar beauty of
this apparatus is that the
time of contact between
ozone and water can be
regulated to a nicety. Sup-
pose we close the outlet
valve 2; then the time of
contact is infinite; a valve
fully opened is the other
limit of least time of con-
tact.

The velocity of the water
evidently can be regulated
so as to suit the purpose,
but so can the amount of

FIG. 52.—Vosmaer Sterilizer.

ozone. Its upward speed is on the one hand regulated by the ordinary buoyancy and on the other hand checked by the downward motion of the water; if this is very great it may be that the bubbles seem to float.

In no other sterilizing apparatus is it possible to regulate the velocity of the ozone by means of the velocity of the water.

If equilibrium is once established between the inlet and outlet, which does not require more than a couple of minutes, there is no reason why it should be disturbed; any accidental increase in inlet will be compensated by a more rapid flow out as a result of increase of pressure or head and any decrease will be checked by less outflow, so that in actual practice one has never to pay attention to the apparatus, it is absolutely self-controlled.

As for the sake of highest economy, it is necessary that the standpipe should be completely filled with a homogeneous mixture of ozone and water, it is evident that the cross-section should be in due proportion to the amount of mixture running through. Experience should be the guide here, not merely conjecture.

As already stated, we made an experimental sterilizer of glass in order to learn all there is in it, and later to show other people its wonderful working. It had a diameter of one foot and a height of 33 feet.

Making the diameter a little over three times larger means an increase in capacity of ten-fold; the one foot will take care of about 10,000 gallons per hour, thus the second-named size will handle 100,000 gallons per hour.

Of course, for regular work we would not advise the making of a large standpipe of glass; any other material will do, and thus it goes without saying that one made of steel plate will be the cheapest.

There are a number of acid-proof paints that may be used as an inside coating that will stand the action of ozone; any one of the kind that belongs to the tar family will answer the purpose very well.

In Figs. 53, 54, 55, and 56, we give reproductions of standpipes that we have used. In 53 we see side by side the glass one foot diameter outside and the iron two feet inside the wooden scaffolding hiding a staircase.

This cut shows the two-foot tower delivering its water. In
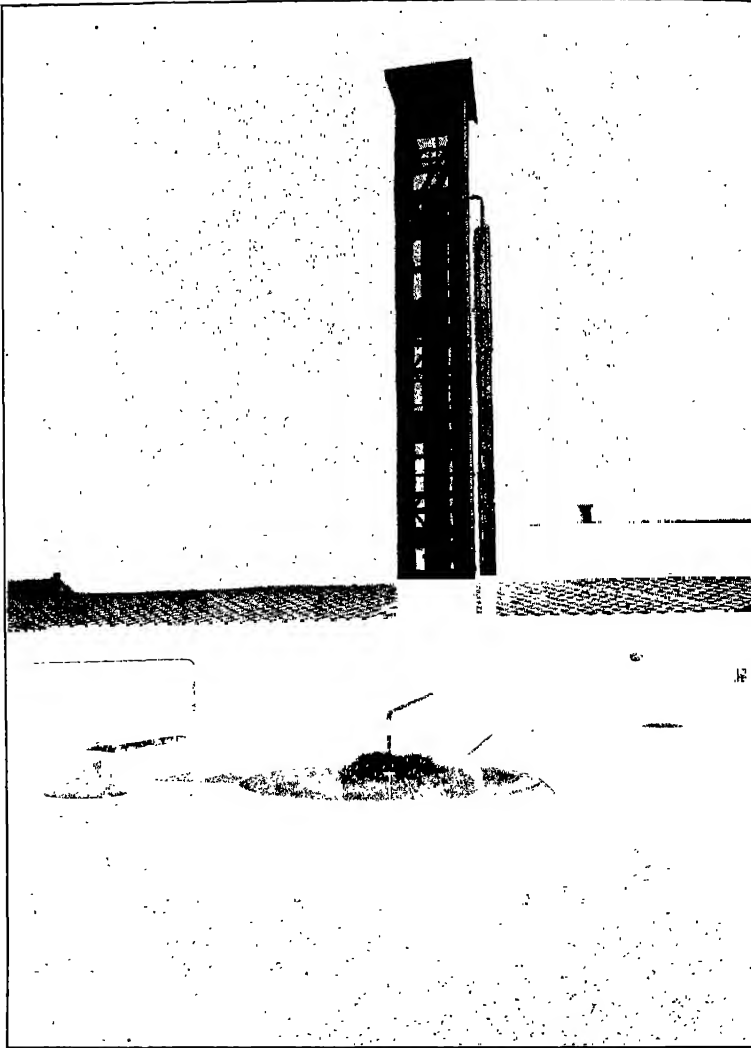
FIG. 53.—Vosmaer Sterilizer.
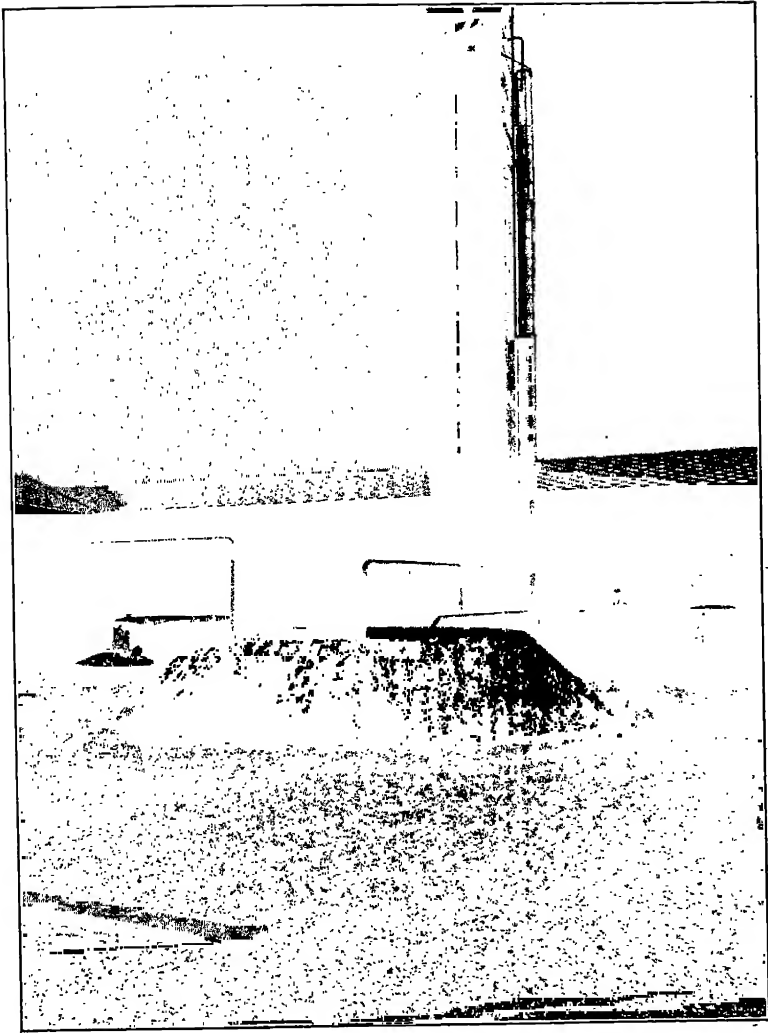
Fig. 54.—Vosmaer Sterilizer.
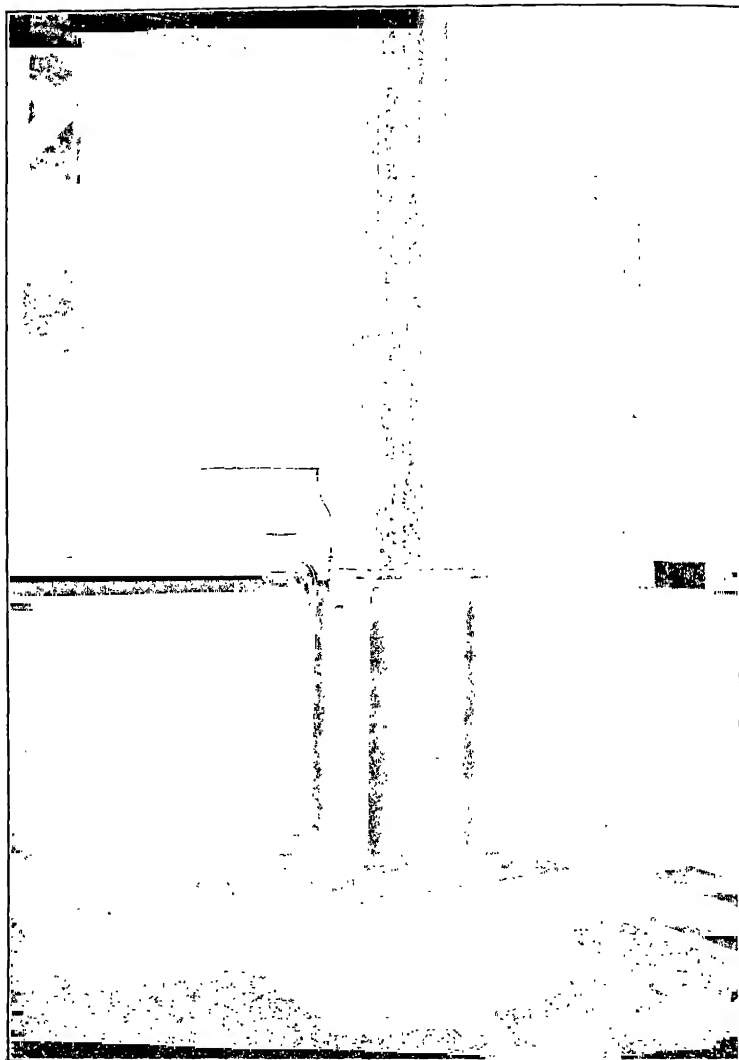
FIG. 55.—Bottom Part of Vosmaer Sterilizer.

Fig. 54 we see the smaller one at work. The respective capacities were 20 cubic meters per hour for the smaller and 80 for the larger.

The water treated was very bad, titrating over 20 and sometimes even over a 30 permanganate.

Fig. 55 shows the bottom part of the glass sterilizer.

In Fig. 56 are shown two standpipes of the experimental plant in Philadelphia in 1905 side by side, the smaller glass one in front, the larger iron one in the rear. This latter had a diameter of 3 feet and handled 200 cubic meters per hour, that is about 50,000 gallons.

The height of the standpipe is another question to consider; as the height also determines the time of contact. Now for a water of good quality we do not want much ozone to sterilize it; that means that we cannot get our time of contact through having a large diameter of standpipe, thereby having a low speed of downward flow, and hence in that case we are to make up for it by increasing the height.

We wish particularly to emphasize the necessity of true harmony between all the different items; anyone not familiar with all these details, which have never been published before, is bound to make blunders.

A most important question to consider is that of height; it does not mean loss of head, because the water leaving the standpipe at the bottom is still under the same head; what we really do lose is the energy spent through friction.

Some outsiders have calculated that our standpipe caused a loss of head equivalent to its height. That is a mistake; we do not lose more than a few feet, due, as said, to frictional losses in piping, etc.

Instead of keeping up the level of the water at the top by means of a check-valve 2, at the bottom, we may as well do so by having the water come out at a higher level as sketched in Fig. 57.

It may be said here that none of the other existing devices allow of that, and when we have in mind the pumping up of large volumes of water it does make quite some difference whether the head be some 5 feet or 20 feet.

If locality allows, our sterilizing standpipe can be sunk in a pit, so as not to have to lift the water if there is no chance of utilizing the pressure.
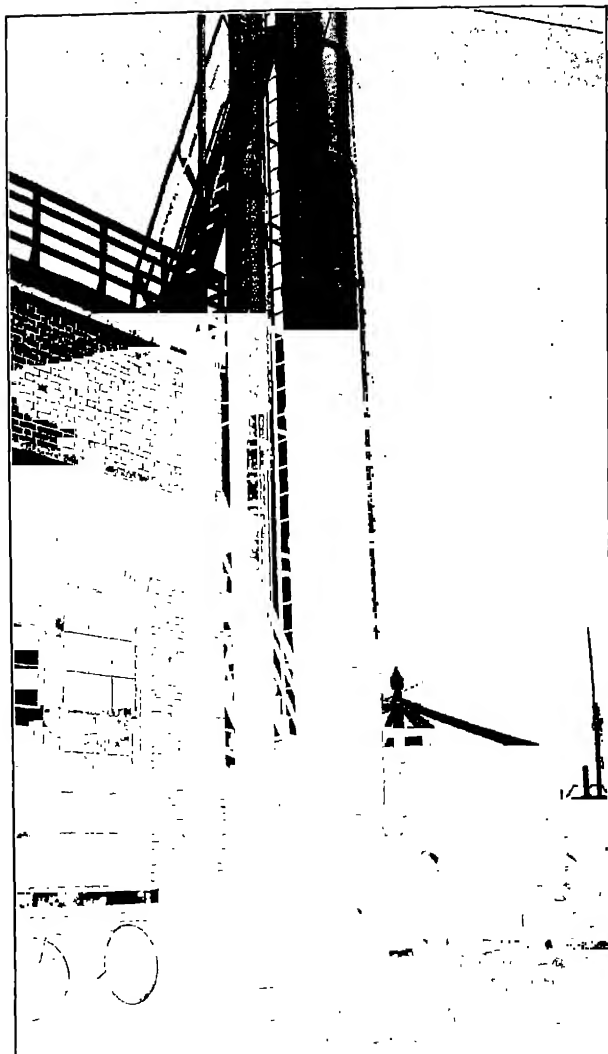
Fig. 56.—Vosmaer Sterilizer.

The popular saying, that the proof of the pudding is in its eating, may be quoted here and adapted to our sterilizing apparatus.

In the year 1905 (May 19th) Drs. Hale and Jackson of the New York Department of Water Supply made some tests with it, that is, with a standpipe of 1 foot diameter and with one of 3 feet diameter.

They took samples of the water as it entered the top of the apparatus, and at the bottom where it escaped.

The water, a rough-strained water from the Schuylkill River in Philadelphia, contained organic matter equivalent to 14.5 and 10.7 permanganate of potassium respectively, and carried no less than 567,000 and 665,000 bacteria respectively at the inlet and 83 and 15 respectively at the outlet, a reduction of 99.985 and 99.998 per cent respectively in bacteria and 100 per cent when considering *B. coli* only.

The treatment further showed up to 80 per cent reduction in turbidity, up to 77 per cent reduction in color, 11.4 per cent reduction in albuminoid ammonia, 79.5 per cent in nitrites, and up to 40 per cent in organic matter in solution.
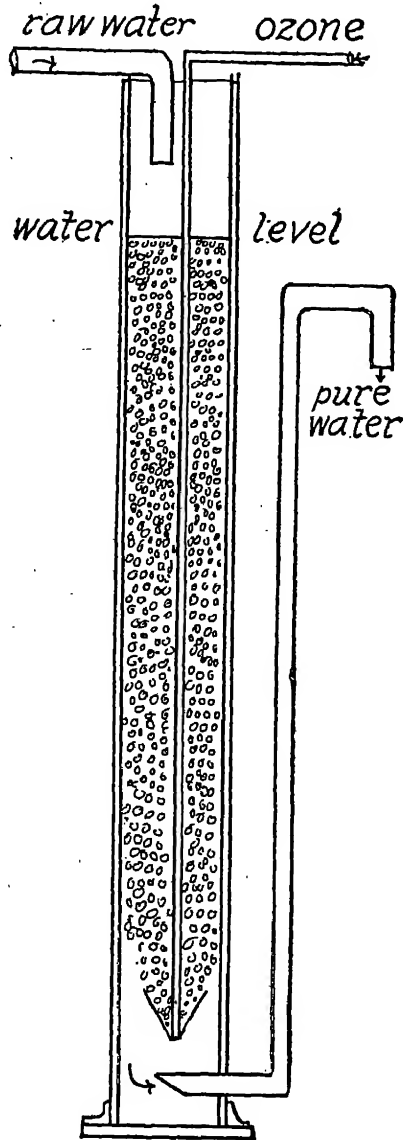
FIG. 57.—Vosmaer Sterilizer.

The quantity of water treated for this test was 5000 gallons per hour and the ozone supply was 5600 cu.ft. at a concentration of 1.3 gm. per cubic meter. These figures are officially given; the report of Dr. Rivas, then assistant bacteriologist of the water department of the city of Philadelphia, is as favorable. The efficiency of the sterilizing apparatus showed itself clearly when we tried the result of ozone on the raw river water (unstrained).

It carried up to 2,500,000 of bacteria per cubic centimeter, sometimes, but on this occasion no more than 1,100,000; this number was reduced to 460 up to 1500 by different rates of treatment!

These figures are intended to illustrate the efficiency of the sterilizing apparatus as described, the action of ozone by itself having been proven so often that we need not insist upon that.

In Fig. 57 we give our sterilizing apparatus in its latest development and wish to emphasize that perfect harmony between the different items is essential to perfect work.

The most simple of all arrangements to bring the water in contact with ozone is the Otto emulsifier; that is, the application of the well-known injector for the purpose mentioned.

Here the water under pressure accomplishes the double duty of drawing the ozone and mixing it thoroughly. This mode of sterilizer appeals to everybody.

Its defects, however, are, first, that there is no possibility of a close regulation of the ratio between water and ozone; then in the second place the tremendous excess of water over the ozone, so that a very strong ozone has to be used, and that is more expensive pro rata than a weaker concentration. The third objection is the extremely short time of contact between both agents, instead of the desirable long time of contact; and as a fourth drawback, we can mention the fact that the contact though apparently very intimate, is not such at all.

Practically all this means that in addition to the emulsifier one has to use some kind of a standpipe again, and that is what is done in all the Otto plants in Europe; there are quite a good many of them but the emulsifier is not the best part of them.

We must draw attention here again to the saying that all the European plants give full satisfaction as to bacteriological results; the question of economy, however, is apart from the

success as a whole. After all ozone is not so very expensive and even if some more of it is being used than would be necessary when some details were changed, it does not influence the cost of the water so very much, the total expense being made up of different items.

There is yet one more method of applying ozone to water. It is to have a large compartment filled with strong ozone and inject water into it in an extremely fine spray such as is obtained from so-called atomizers.

This method is one that appeals to many people but it is no good at all; there is not one good feature in it. First of all to inject water as a fine spray costs much energy; it is the surface tension that plays such an important rôle here. Atomizing, as it is called, requires a very high pressure of the water and that is very expensive.

The well-known firm of Koerting, who have been in the field with injectors and sprays since these were invented, ask a pressure of 90 lbs. per square inch for their atomizers.

All that high pressure is absolutely lost, the energy spent being converted into heat; that is another drawback, as we do not wish a rise in temperature, however small it may be.

The extremely fine drops of water, seen as a dense mist, are yet very large compared with the size of the bacteria; they have only their surface to offer for action and this surface increases rapidly through conglomeration of small drops to larger ones.

The time of contact is very short indeed; the mist, however fine, will very soon degenerate into a fine rain and the drops will not keep in the ozone atmosphere but fall to the ground.

If we could keep the water as a mist in the atmosphere of strong ozone and for some time, then the method might have some good points; as it is now there is nothing in it at all and the trials have all resulted in so many failures.

Just a little physical reasoning beforehand might have warned the experimenters against complete failure.

It is a pity there has been so much energy and money wasted on experiments in finding out the best way to apply the ozone to the water; the problem is so very simple indeed and it only requires a thorough understanding of the known facts about common things, whereas the manufacture of ozone indeed is, or rather was, a very difficult problem.

The rational application of ozone in other industries than the purification of water is not so very simple. Every case will have to find its own best method.

Up to now we have not said a word about the question of turbidity of the water, and though it does not belong to the domain of ozone we might remind the reader that as turbidity is chiefly caused by mineral matter in a very fine state of dispersion, ozone cannot affect it and a preliminary filtration or clarification of the water has to be gone through; in some cases just a rough straining or settling may suit the purpose.

It is impossible to enter into details regarding this purely engineering problem, but we wish to call attention to the large difference there is between a rough straining filtration and a bacteriological filtration. The speed of filtration may in the first case be about ten to twenty times that of the latter.

There is no reason to use coagulants unless the turbidity is caused by extremely fine clay in suspension, but this case is not a rule but an exception.

It is unnecessary to use coagulants in conjunction with proper ozone treatment, as there is no reason to do so unless in the case cited.

All we need to do so as to free the water from matter in suspension, is to filter it as rapidly as possible, or strain it by means of centrifugal force. This latter method seems very promising in certain cases and has several advantages over so-called mechanical filtration as, for instance, there is no need for cleaning, no waste water and no clogging, etc.

The controlling of the regular working of an ozone water purification plant is no difficult matter, as there is nothing to get out of order except the ozonator, which accidentally might suffer from a breakdown of one element.

This accident would show at once on the switchboard.

As long as the machine runs at its own speed, there is no reason why the tension should change, and as long as this is fairly constant, there is no reason why the amperage should change, unless as already stated there is some element out of action, and as long as those two remain fairly constant there is no reason for the wattmeter not to show its regular point. That is all one has to look at.

As long as the wattage remains the same, as it usually does,

one need not bother about the ozone, that is all right. Of course the compressor is supposed to run its regular number of revolutions.

As long as the ozone supply is right, there is no need for troubling about its effect, because it will do its work with great regularity.

The only point worthy of consideration is the quality of the water, which may vary a great deal.

The determination of the content of organic matter in solution does not take a very long time and the practical check to be sure there is not a lack of ozone is to make sure there is an excess of it, and a very slight one will be easily detected by smelling, the olfactory nerve being very sensitive indeed to ozone. The whole process is so remarkably simple and self-contained that hardly any attendance is required.

If the quality of the water changes say in the direction of getting worse, then all we have to do is either increase the amount of ozone by having more ozonators at work, or decrease the quantity of water.

There should be so much ozone capacity that there always can be an excess of ozone.

If for reasons of interest or of control, a daily report is required, to contain determinations of different items and the concentration of ozone and the yield per kilowatt hour are mentioned, it will be evident that there is very little change in the figures. We have had our plants running for days and days without any change at all, there being a remarkable regularity in the working of all the different parts.

Bacteriological tests will show the same regularity as long as the quality of the water does not vary very much. It takes two days to be sure about bacteria, but it takes no more than half an hour to make a test for the reduction percentage in organic matter, and that is just as sure a guide as the bacteriological test. As long as the regular reduction is obtained, so long will the bacterial result be the same, no matter what their original number was.

The question of cost is a delicate one; it depends so very much on the size of the plant and local circumstances that it would not be fair to the system as such, were we to give definite data.

Yet it is desirable to give the reader some idea of the cost.

Taking it for granted that a water of an average quality, say requiring no more than 10 mg. of permanganate of potassium for its organic matter in solution, can be satisfactorily treated with no more ozone than one part in a million, this means that when we also take it for granted that modern ozonators yield at least 50 gm. of ozone per kilowatt hour, we require about 80 kilowatts for a million gallons per hour, or let us take 8 kilowatts for 100,000 gallons per hour.

Now to this figure there has to be added the energy required to force the ozone into the water, and also that required to pump the water against a head of about 6 feet.

As a rough estimation we may take those two together to be about 12 kilowatts, which means that for the generation of ozone and its application there are needed about 20 kilowatts per 100,000 gallons of water treated per hour. A common mistake is to take the price of a kilowatt-hour as that for which some corporation sells it. There is a great difference between cost of a kilowatt and its selling price, and more especially so when the generator is fully loaded every day, and during the whole day.

The cost may be as low as one cent under favorable conditions, even for a comparatively small plant, and if we consider a 1,000,000 gallon per hour plant, the cost of treatment would not have to exceed $2.00, and may be in the neighborhood of $1.00, not including interest, depreciation, and general expenses of plant; of course, these items cannot be estimated in a general way.

These figures are merely given to show the reader that the enthusiasm about ozone is not a dream but a feasible thing, based upon actual performance in a great many places in Europe on very different scales and under widely different conditions.

Other methods of purification. Although not belonging to the scope of this book, some other methods of water purification may be discussed in a few words so as to throw full light on the advantages of ozone for this purpose.

In Europe there is practically no other method than the old-fashioned and very satisfactory one of slow sand filtration, in competition with ozone for modern plants.

Such chemicals as sulphate of copper, hypochlorite of lime, chlorine, or others, have no chance whatever to be taken into

consideration in any of the more civilized countries. Not even the old alum method is being used there to an extent worth speaking of, except as a means of clarifying a very turbid water, as this occasionally occurs during some days of the year. As to copper sulphate as a means of sterilizing drinking water, it sounds most horrible to anyone from the other side; it has not a single advantage over other methods, and its introduction by Moore in 1905 may be considered a deplorable mistake.

Lime added to water certainly does kill intestinal bacteria; the coli and typhoid seem to want free carbonic acid to live on, and that is taken away by lime. The disadvantages are the very long time required to do the work—five to twenty-four hours—and the increase in hardness of the water, which is very unpleasant, if not unwholesome.

The use of alum is so well known here that it needs no discussion; alum when in proper quantity certainly does remove the greater part of the bacteria through precipitation. Its disadvantages are the necessity of an excess, so as to be sure of no shortcoming, and the uncertainty of a homogeneous mixture. Chloride of lime, or rather the hypochlorite, acts on water through its contents of chlorine gas and its lime.

Chlorine gas acts on water in very different ways; the reaction is far more complicated than just liberating oxygen *in statu nascendi* from the water.

The disadvantages are the highly noxious properties of chlorine, the very disagreeable smell and taste and the absolute impossibility to apply it in a satisfactory way, so that every part of the water be treated. Chlorine gas is as bad for the purpose. It is not an easy engineering problem to make a thoroughly homogeneous mixture of very large volumes of water with very small volumes of something else.

As to the respective costs of all these different treatments, it is hard to give strictly comparable figures. The Engineering Record, of 1913, page 16, states the price of the chlorine treatment to be $3.75 to $19.00 for bad waters, and between $1.75 and $5.60 for ordinary waters.

We should leave out the question of cost when we have to consider matters of health.

The chlorine method certainly has not the advantage of the excess of oxygen in the water after treatment, but over the

ozone treatment it has the advantage of a far cheaper installation, so that even if the cost does come so much higher when considering treatment only, still it may be cheaper when the additional expenses for sinking fund are also considered.

Chlorine may be very good for the treatment of sewage, but for drinking water it is no serious competitor with ozone, when we look for *quality* of result.

There is still one other method, and that is the one of treatment with ultraviolet rays. This, indeed, seems to be very efficient, and very simple, too.

It is said on the one hand that 15 kilowatts will take care of 1,000,000 gallons; that would be very efficient, but it is also said that impartial and official tests have not been as favorable as the claims made by tradespeople.

There is one very great drawback against its use—that is the extreme sensibility to turbidity. Good results have been obtained, there is no doubt about that, but on perfectly clear water; even a trace of turbidity reduces the effect in a very marked way, and to such an extent that at a very slight turbidity the effect is *nil*.

This defect, not of the system but of the ray itself, cannot be corrected, since it is fundamental—it belongs to its nature.

Still the ultraviolet ray treatment of water is one worthy of consideration. It is interesting to know that for the Petrograd water supply an ozone plant and an ultraviolet ray plant were running in competition. The first has been a complete success, the second an absolute failure, merely on account of the turbidity of the water.

Proposals of treating drinking water with peroxide of chlorine (ClO_3) or peroxide of hydrogen, H_2O_2, need no further consideration.

Ozone Water Works. It will be expected from a book of this kind that the existing ozone plants be now described. There are a great many of them in Europe, furnishing many evidences of success of the system as such, and most of the installations or perhaps all of them have been described in some periodical, the first ones in detail, those of more recent date less and less detailed, because everyone interested in the matter is well informed concerning it by this time.

The list given below is intended to show that if we do speak of a complete success of the process in Europe, it is not without

PARTIAL LIST OF EUROPEAN PLANTS FOR THE STERILIZATION
OF DRINKING WATER BY MEANS OF OZONE

Name of Town.		Date of Installation.	Gallons Water Treated per 24 Hours.
FRANCE:			
Marseilles............	Mediterranean Brewery.	1902	129,600
Marseilles............	Electrical Exposition....	1908	64,800
Marseilles............	Municipal Plant........	1910	75,600
Nice................	Municipal...............		
Nice................	Bon Voyage Plant......	1905	6,480,000
Nice................	Rimiez Plant..........	1909	3,780,000
Cosne...............	Municipal.............	1906	648,000
Paris................	Municipal.............	1907	648,000
Paris................	St. Maur Plant........	1910	24,100,000
Dinard..............	Municipal.............	1907	135,000
Dinard..............	Municipal.............	1909	162,000
Chartres............	Municipal.............	1908	1,620,000
Armentières.........	Municipal.............	1909	972,000
Avranches..........	Municipal.............	1912	621,000
Saint-Brieuc........	Municipal.............	1909	810,000
Saint-Servan........	Municipal.............	1911	1,350,000
Laval...............	Municipal.............	1912	1,620,000
Les Sables-d'Olonne....	....	1911	675,000
Villefranche.........	....	1911	7,020,000
Indret..............	....	1903	19,440
Toulon..............	Arsenal (5 Plants).....	1910	194,400
Toulon..............	Arsenal (1 Plant)......	1912	38,880
Sotteville-lès-Rouen....	Municipal.............	1911	648,000
Lunéville...........	Municipal.............	1912	2,025,000
Compiègne..........	Municipal.............	1911	1,620,000
Lorient.............	Municipal.............	1911	2,700,000
ROUMANIA:			
Sulina..............	Municipal.............	....	405,000
Turnu-Severin.......	Municipal.............	....	1,080,000
Constantza.:.......	Municipal.............	....	1,620,000
Pietra-Neamt........	Municipal.............	....	1,188,000
GERMANY:			
Wiesbaden..........	Municipal.	....	1,080,000
Paderborn..........	Municipal.............	1902	675,000
Chemnitz...........	Municipal.............	....	972,000
Leipzig.............	Ribeck Brewery.......	....	64,800
Hamburg...........	Palmin-Werke Schlink. .	....	64,800
Hermannstadt.......	Municipal.............	....	972,000
Munich.............	Augustiner Brewery....	....	64,800

Name of Town.		Date of Installation.	Gallons Water Treated per 24 Hours.
ITALY:			
Pontelongo..........	Municipal.............	....	64,800
Ravenna............	Municipal.............	....	32,400
Spezzia..............	Municipal.............	....	810,000
Florence............	Municipal.............	....	1,350,000
Rovigo.............	Municipal.............	....	540,000
Genua..............	....	....	360,000
RUSSIA:			
Ekaterinovka........	Mines Service.........	....	162,000
Petrograd...........	Trial Plant...........	....	324,000
Petrograd...........	Municipal.............	1910	14,040,000
AUSTRIA:			
Braïla..............	....	....	175,000
SPAIN:			
Madrid.............	Municipal.............	1911	189,000
SOUTH AMERICA:			
Ribeirao-Preto, Brazil.	....	....	324,000
Buenos-Ayres........	....	....	64,800
Valparaiso...........	....	....	64,800
Total joint daily capacity of above plants in gals. per 24 hrs.			84,843,920

substantial evidence. This list, taken from the report by Russell Spaulding on the application of ozone to water purification, enumerates 49 ozone plants with a total daily capacity of over 84,000,000 gallons, and one may take it for granted that such places as Petrograd and Paris do not adopt a system of water purification unless it has proved to be reliable.

All the installations have been erected by and are using ozonators of the Siemens & Halske, the Abraham-Marmier or the Otto companies; most of them use the Otto emulsifier in conjunction with some other system.

It certainly would be superfluous to go into details about these plants; they have been described over and over again; a few remarks, however, may be made.

The Paris plant has not been installed, but after a whole year's trial the success of the competing plants can be best judged from the fact that the city allowed a plant for the treatment

of 12,000,000 gallons daily to be erected by the Siemens people, and one as large by the Otto people. Fig. 58 gives an idea of the general arrangement.

On the left side there are the Otto-Abraham-Marmier ozonators arranged in five sets, each containing four units made of four double discharging plates. The voltage is 12,000.

On the right-hand side there are eight groups of Siemens ozonators, each having ten units of six tubes. The voltage is 6500.

The total energy supplied of 80 kilowatts for each is capable of generating $2\times80\times50=8000$ gm. of ozone of high concentration per hour, namely 3 gm. per cubic meter.

The ozonization of 1 cubic meter of water requires about thrity watt hours. The handling of the water is in addition to this.

There are ten towers each supplied with four emulsifiers; time of contact between ozone and water is about three minutes.

As we have said before the emulsifier is not the best part of the plant; it requires a highly concentrated ozone (3 gm. per cubic meter) and it requires an additional apparatus, called tower, to finish the work which it could not do; that is one reason why we prefer an apparatus without an emulsifier. We must repeat here that all the plants in Europe give entire satisfaction, so if we say anything against the use of the emulsifier, it is not that it does not do the work satisfactorily, but only that we claim to be able to do the same work at less cost.

The Petrograd plant is another large one, designed for 14,000,000 gallons and is to be enlarged for another 24,000,000.

Fig. 59 gives a view of the 126 Siemens type ozonators running on 500-period, 7000-volt current.

It would be simple indeed to copy testimonials of trials; they are too numerous, however, and too monotonous also, all coming down to the point that the result leaves nothing to be desired.

Altogether different from the water ozonization on a large scale is that done on a small scale for individual use.

The Neel-Armstrong Co. arranged an apparatus so that the movement of a push handle is sufficient to, in the first place, start the ozonator and in the second place the water supply.

The ozone required to do the work is drawn in by the water itself by means of the well-known injector type, a thorough mix-
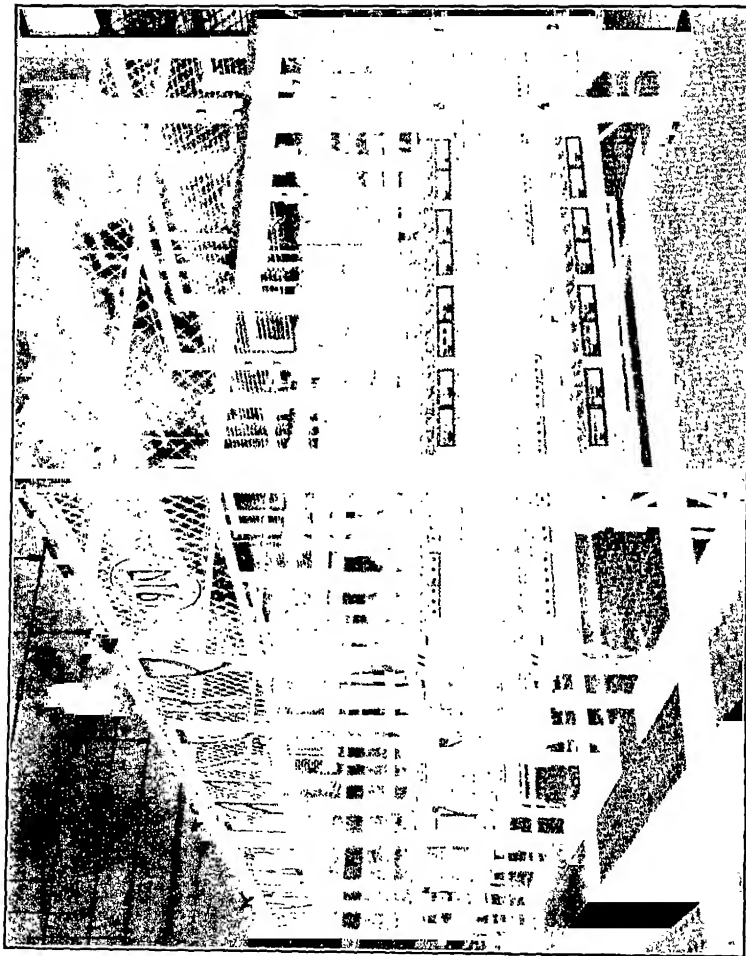
Fig. 59.—Battery of Siemens-Halske Ozonators in Paris.

ture of water and ozone being accomplished in a mixing device of special design.

The company guarantees the water to be free from pathogenic bacteria.

This so-called household apparatus seems to suit the purpose remarkably well. They are made in different sizes up to 30 gallons, and meet a long-felt demand.

Of course the water has to pass through some filtering medium before being subjected to the ozone treatment.

One detail should be mentioned, the ozonization works, so to say, instantaneously, but of course the filter does not; to make up for the difference in time, there is a storage tank for the filtered water (not for the ozonized). As the demand for purified water is not continuous, the storage tank accumulates the supply of the filter and according to its size will allow of drawing water any time and in any quantity within the limits of reasonable demand (from one glassful to 30 gallons at a time).

The Neel-Armstrong ozonator is of the original von Babo type, metallic wires enclosed in glass tubes. It presents the good features of electrodes sealed in vacuum, the use of a special Bohemian glass, and glass of uniform wall thickness.

When speaking of the Otto emulsifier system of bringing water into contact with the ozone, we did not say much in favor of it. Now here in this case of a household water purifier we are in favor of the very same principle of using an injector as a means of mixing.

There is no inconsistency in these different opinions of one and the same device; for a household apparatus efficiency is of very little, and simplicity of the utmost importance, whereas for industrial use or the purification on a large scale, it is just the reverse—economy in working is of the greater importance.

If we want to drink a glass of pure water it matters very little indeed whether the ozonization costs one-hundred-thousandth of a cent or a thousand times that, but for a municipal water supply it matters very much indeed whether the cost is $2 per million gallons or $2000!

CHAPTER XIV

PURIFICATION OF AIR BY OZONE PROCESS

THE next best thing to pure water is pure air; we can all get that free of charge in the country, but then most people cannot afford that luxury and hence have to do with the air we are getting in cities.

The importance, taken from a commercial standpoint, of the purification of water over that of air lies in the fact that neglect of the first is punished at once, whereas it may take years and years to make it evident that bad air may also lead to disease.

The use of contaminated water may, and probably in most cases will, lead to disease, eventually to death, and that is why people should drink pure water rather than impure.

The cases of typhoid are many; the death rate is about 10 per cent and so there are many people who either in their own family or among their friends know of cases of typhoid.

Many people are aware of the menace from water, but few of them realize that inhaling foul air may also be injurious to health. The trouble is that it takes such a long time for bad air to manifest itself as an injury, whereas one glass of water infected by *B. typhosis* will almost in all cases cause the person who drank it to catch that disease, but we may inhale filthy air for hours and for days without acute effect on our system.

It is a strange fact that so many people speak about fresh air and so few realize that during the office or business hours they do not seem to care much for it.

The trouble is that one soon gets used to bad air, and bad odors are apt not to be noticed after a while; but the fact remains that pure air is more wholesome than contaminated air. In our regular daily great city life it is almost an impossibility to provide for fresh air. No amount of ventilation, not even an otherwise unbearable draught, will be capable of keeping a crowded room or place in good condition unless one takes recourse to ventilating with ozonized air.

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The chemical composition of the atmosphere is nearly the same all over the world, viz., oxygen 20.99 per cent, nitrogen 78.03 per cent, inert gases 0.95, carbon dioxide 0.03 per cent, all by volume.

Expired air contains about 16 per cent of oxygen, but that does not mean that we can breathe the same air four times; air with less than 18 per cent of oxygen is not breathable, but fortunately there is always so much excess of air over what we actually need that there is hardly ever danger from suffocation through lack of oxygen.

The amount of air taken in at each breath varies according to capacity of lung and deepness of breath. For adults it is between 1000 and 4000 c.c.; as a rule it is about 1000; that is 1 liter, and as there are a thousand liters to the cubic meter, that volume of air would do for about one hour, but it certainly would not produce a pleasant feeling.

Expired breath contains about 4 per cent of carbon dioxide— another reason why expired air is not breathable, about 1 per cent being the limit; but here again there is no danger coming from that source either, because the diffusion of gases and their mixing through agitation in the air is rapid enough to result in a fairly homogeneous mixture.

There was a time when the theory was held that human beings gave off volatile organic toxines, but it has been definitely settled that this is not the case, and yet nobody will contradict the statement that too many people in a confined space cause an unpleasant feeling of closeness.

This is partly due to temperature and moisture that is abnormal, but even if we take that objection away, the uncomfortable feeling remains.

The theory that harmful bacteria might have something to do with it has also been dropped; probably the effect is due wholly to psychological influence on physiological functions. In this case we may hold the disagreeable odors as resulting from respiration, and perspiration responsible for the disagreeable feeling.

It is perfectly safe to say that all these factors are absolutely harmless in a direct way, but they are not in an indirect way, because when we stay in a place where there are bad odors, we are apt to restrict our breathing.

When in the country it is not so much the quality of the

air as such, that does us so much good, as the fact that its freshness causes us to breathe freely and deeply.

Modern methods of lung exercise have taught us the benefit to be derived from deep breathing as a means of developing our lung capacity.

Our olfactory sense is very delicate; that is, very small amounts of odors may be detected (one part of asafoetida in a thousand million million parts of air is detectable) and hence it is that no amount of ventilation by itself will be capable of sweeping out bad odors, so much less as they are being made anew continuously by everyone present in the room or space.

Removal of bad odors by means of air-flushing is an absolute impossibility, and yet they should be removed. That is where ozone comes in; ozone will take care of bad odors in a very effective way by oxidizing them to odorless carbon dioxide and other compounds.

The method of purifying air by ozone has the advantage of being fully reliable, very efficient and inexpensive, as we shall learn presently.

There are people who maintain that ozone will not take away bad odors, but only masks them; they actually consider their view proved by the fact that if in a room the bad odors have been taken away by ozone and the ozone supply is stopped, then the bad odor will be noticed again in a short time; that is quite true, but is not a proof. On the contrary, bad odors, like all odors, are strongly adherent to all sorts of material, especially clothes, wall-paper, upholsterings, carpets, all wooden and other furniture, so no wonder that as soon as the ozone supply is stopped the bad odors return again; that is, not the same odors come back, but new ones.

Dr. Milton Franklin has performed some scientific experiments in this matter and has proved beyond doubt that bad odors are destroyed, completely destroyed, by ozone, and this is not surprising, if we remember the extraordinary oxidizing property of ozone. A substance that is capable of oxidizing sulphur dioxide to trioxide, sulphuretted hydrogen to sulphurous acid, and so on, most certainly will be in a position to oxidize the delicate organic volatile matter present in expired air.

Dr. Franklin's experiments have settled this question in a

conclusive way. The next point to be considered is this, will ozone kill moulds and bacteria in air?

To a certain extent it will, as has been shown by the experiments of Dr. Olsen, but ozone in the concentration that is breathable, say of about one part in 10,000,000, will not do much good in that direction.

Dry ozone in dry air has very little, if any, effect on dry bacteria, but we do not care for dry air bacteria; they are harm-
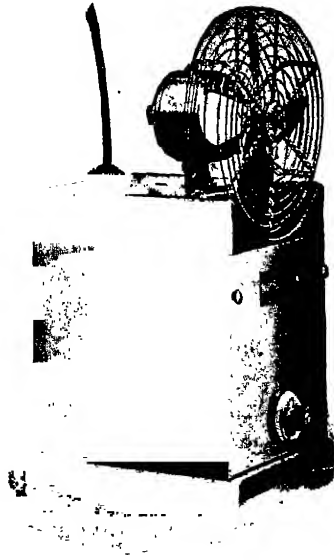
FIG. 60.—G. E. Co. Ventilation Ozonator.

less and that is our good fortune too, for every day we take in millions of them.

There is no reason to be afraid of bacteria in general; only those that cause disease should be avoided.

But we also must bear in mind that our ordinary air is dust laden. Now bacteria cling to particles of dust, so much the more as these also are centers for condensation of moisture.

Droplets of moisture are spread into the room through coughing and sneezing, and that is why the experiments of Dr. Olsen taken with schoolroom air show such good results as to the effect of ozone on bacterial and mould life, we em-

phatically advise the reader interested in school hygiene to read Dr. Olsen's report and also his article on ozone in ventilation. The evidence given is conclusive, and should be taken to heart by parents and every one caring for good health.

The object of ventilating with ozonized air is not in the first place to try to kill bacterial life; the real object is to take away the bad odors and by so doing remove the uncomfortable feeling one experiences when remaining for a long time in a confined space.
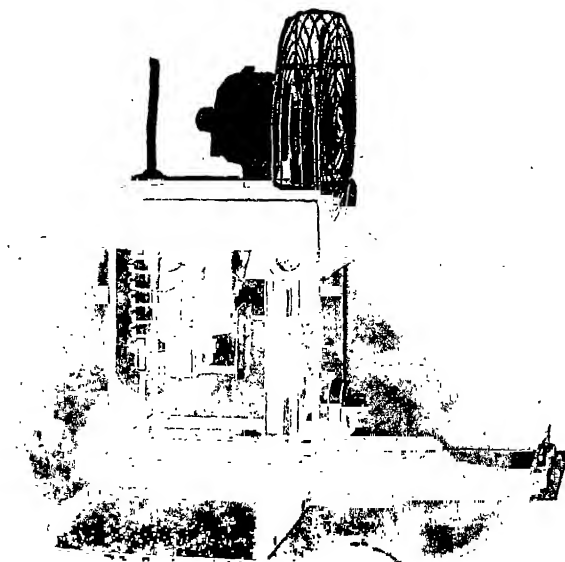
FIG. 61.—G. E. Co. Ventilation Ozonator.

We do not at all intend to supplant ventilation by ozonization, but to supplement it, leaving to ventilation what it can do and perfect this by what it cannot do. The uncontested invigorating power of ozone when inhaled is an additional benefit, not to be taken too seriously, because proper ozone ventilation should be done in such a way that there hardly is any excess of ozone.

Strange to say, some people object to the peculiar smell of ozone and to avoid the chance of this it is better not to have an excess. The proof of the right dose of ozone lies in the fact of not being noticed.

The great question, generally overlooked by those who want to say something against the use of ozone for ventilating purposes, is the right concentration. It should be very low, not about 20 mg. per cubic meter, but certainly not more than one m.gr. and preferably even less, down to one-tenth of this amount.

In overdoses, ozone, like any other substance, is liable to do more harm than good; the beauty of its use lies in the fact that it is so powerful that one need not have strong doses. We
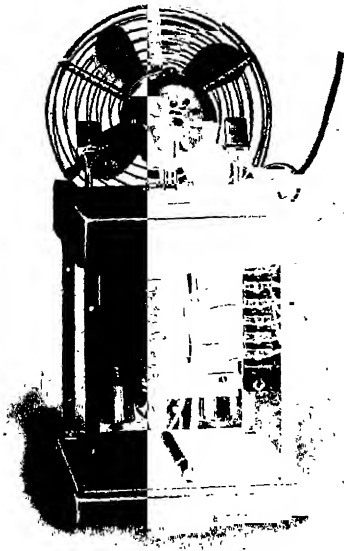
FIG. 62.   FIG. 63.
G. E. Co. Ventilation Ozonator.   G. E. Co. Ventilation Ozonator.

have mentioned that for the purpose of sterilization of water a concentration of 1 gm. per cubic meter serves the purpose if applied in the proper way; now here in case of purification of air one-thousandth of that concentration is enough.

The actual amount of obnoxious volatile substances in vitiated air expressed in milligrams is very small, and it requires but very little ozone to destroy that small quantity. That is the reason that ventilation with ozonized air is so very inexpensive.

One kilowatt produces say at least 100 gm. of ozone, of the very low concentration mentioned, that is 100,000 mg., so if we

want to have no more than 1 in 10,000,000, there should be no less than 1,000,000 cubic meters of air per hour.

A fair ventilation supplies 25 cubic meters of fresh air per capita, so it is evident that the energy of one kilowatt would suffice to invigorate no less than 40,000 people.

From these figures it is evident that ozonators for ventilating purposes are not of the style of kilowatts size but of a few watts size, and it is also evident that the price of ozone manufacture in addition to the usual ventilation can easily be neglected, and it is highly to be regretted that unfair and illogical experiments have led some people to the wrong conclusion that
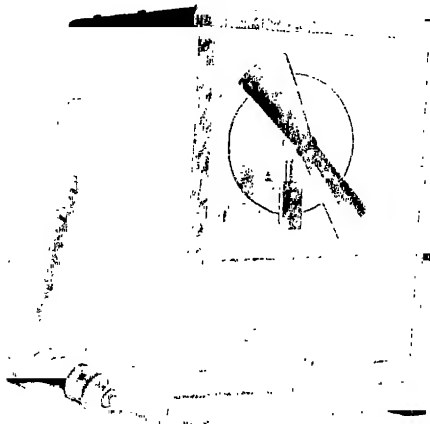
Fig. 64.—Vohr Ventilation Ozonator.

ozone is a dangerous gas. Almost any substance is a poison when taken in a dose that is a hundred times too strong.

Of late five interesting publications on the subject of ozone for ventilation have appeared namely, the address by Ludwig von Kupffer of Berlin at the 9th Congress for Heating and Ventilating at Cologne, Germany, June, 1913; a lecture held by Czaplewsky at the same place and date; the address by Milton W. Franklin, read at the Fourth International Congress on School Hygiene, Buffalo, August, 1913[1]; Dr. J. C. Olsen's

1. Both these publications have been translated by Franklin. The first appeared in the Journal of Industrial and Engineering Chemistry of April, 1914; the second in Metallurgical and Chemical Engineering, of April, 1914, while the third appeared in the Heating and Ventilating Magazine, Oct. and Nov., 1914.

Purification of Air and Water, read at the same Congress and
Dr. Olsen, Ozone in Ventilation.   (T. Ind. Eng. Chem. Vol. 6,
N. 8, p. 6–9, 1914.)

All these reports by fully competent men agree on the points
of desirability of ozone ventilation, that is, ozonization of fresh-
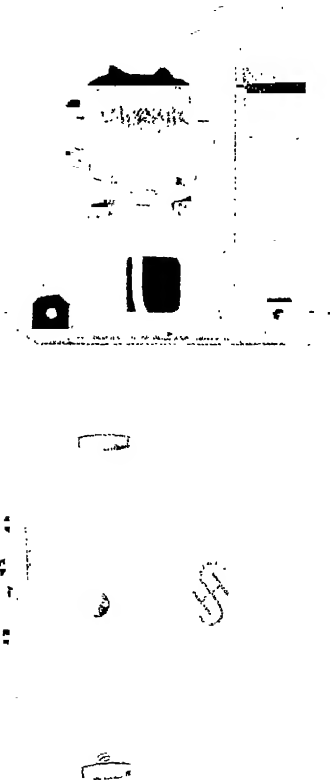
FIG. 65.—Siemens-Halske Ozonator for Ventilation.

air supply rather than ozonization of room air, the benefit to
be derived from ozone, the destruction of odors, and the general
usefulness.

Anyone interested in the matter of ozone ventilation should

read the reports cited; Franklin's, moreover, contains a very valuable list of references on the subject.

We may also call attention to the fact that not only for regular use in office buildings, clubhouses, public buildings, theaters, and such places, is there a demand for ozonization of the air, but also in special cases, such as slaughterhouses, cold storage and warehouses, restaurants, kitchens, toilet rooms, and many others.
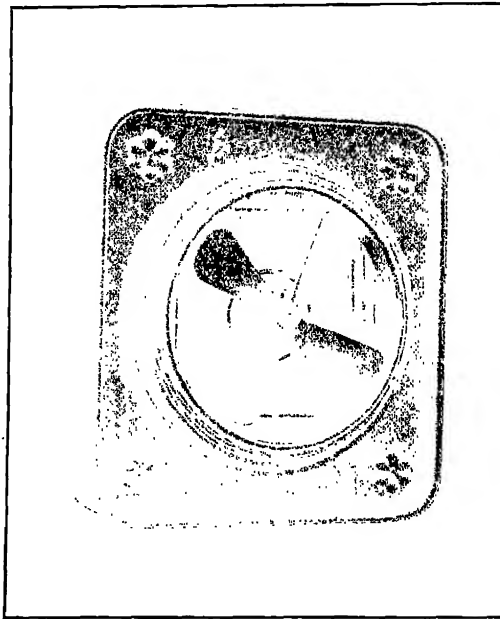
FIG. 66.—Siemens-Halske Ozonator for Ventilation.

Ozonators for this kind of work differ from those intended to give stronger ozone in many ways. The stress put on the dielectric is so low in this case that almost any device will do for an ozonator. There are many makes on the market, but the one preferred by the author is that of the General Electric Co., of which we show some cuts; Figs. 60 to 63 show the newest type. A fan on top of the box draws the air from the bottom through the ozonator tubes and blows ozonized air into the room.

The machine is practically fool-proof, and can very easily be cleaned.   It looks very attractive on account of its size and finish.

That is a trouble for ozonators of this style, viz., the accumu-
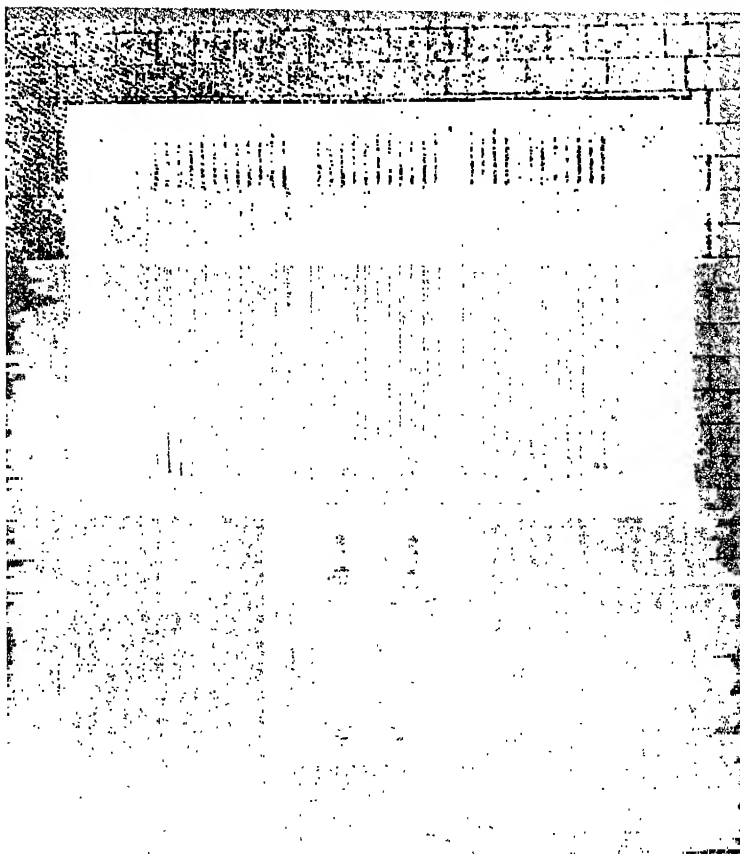
Fig. 67.—Siemens-Halske Ozonator for Ventilation.

lation of dust and dirt on the dielectric; all of them suffer from this evil, except the Vohr[1]), which has the ingenious method of auto cleaning by having a revolving electrode attached to the fan itself and in conjunction therewith a pair of small brushes

[1] Small patent and manufactured by the Hudson Ozone Machine Co.

continuously rubbing against the dielectric, which is in the form
of a ring, concentric with said revolving electrode, see Fig. 64.

Of German make the Siemens are very good again.   In Fig.
65 we give an outside view of an ozonator for about 1000 cubic
meters per hour; inside is their usual tube.   Fig. 66 shows a
handsome model for small capacity, about 50 cubic meters.

For large places it is more convenient to separate ventilator
and ozonators and put this latter in the air ducts.

Fig. 67 shows an unusual type of ozonator, after the style
of a grid.   The catalogue of 1912 mentions some 36 installa-
tions of larger size, the smallest being 1000 cubic meters per
hour, the largest 200,000!   This will do to prove that in Ger-
many, the country of careful scientific investigation, the question
of ozone ventilation has received the consideration it deserves.

Quite apart from the question of the use of ozone as an
addition to the usual ventilation is that of intentional use as
as a therapeutic.

CHAPTER XV

OZONE IN THERAPEUTICS

WE can be very brief on this subject, not because it is not interesting, but because so very little is known about it.

Were we to believe commercial pamphlets or similar literature, we could say that ozone is good for anything.

In 1904 de la Coux published a book on ozone in French, and enumerates favorable results obtained by French doctors as regards the effects of ozone inhalations.

. The therapeutic dose of ozone being about one-tenth of a milligram per cubic meter of air (that is about 1 in 10,000,000) we shall consider his statements that it is one-tenth of a milligram per liter, a quantity 1000 times as great, as a slip of the pen.

The French Drs. Labbé and Oudin seem to have experimented quite a good deal in the line of ozone, and some twenty or more doctors are named that seem to have obtained good results in the treatment of phthisis, bronchitis, whooping cough, catarrh, anemia, chlorosis, diabetes, rheumatism, and gout.

We cannot be too careful in accepting such statements.

What we personally know about the publications of Labbé and Oudin in the line of electro-therapeutics in general, is not of a kind to rely upon, and we had better wait patiently until some institute will take the matter in hand and investigate the alleged beneficial effects of ozone on different diseases.

Our personal experience in this line shows no more than the fact that inhalation of ozone in proper dose increases the percentage of oxyhaemoglobin when this is below normal, and that certainly is an indication that some good may be expected.

It is very much to be regretted that Drs. Jordan and Carlson, also Drs. Sawyer, Beckwith, and Skolfield, when experimenting with ozone, did not work with the proper concentration,

for, having used ozone in up to 200 times the proper strength, they have done much useless work.

We all know that ozone in too strong a concentration will do more harm than benefit; what was, and is, still wanting is an impartial test of ozone in the right concentration or dose.

It is highly probable that ozone administered in the right dose and in the right way, will have a beneficial effect on the course of certain diseases, such as phthisis, chlorosis, obesity, and probably many others. There is no reason why it should not, but it is very unfair and unscientific to test these matters in the wrong way.

Even the possibility of a beneficial effect, if not a cure, for such a terrible disease as tuberculosis of the lung should induce people to test, and certainly since the cost of ozone in quantities of tenths of milligrams per cubic meter of air is trifling. We use 1000 times more for the purification of water, and even that can be done for $1 or $2 per 1,000,000 gallons, so in ozone we could have a remedy at an extremely low cost, the latter a detail of some value.

There are many people who believe that ozone can have no effect on the blood, because, when inhaled, it will all be absorbed by the mucous membranes of the respiratory tract.

This is not the case, however, and those who, like the author, have had occasion to inhale ozone daily, will have experienced effects on the system that are not to be accounted for, if all the ozone were absorbed by mucous membranes of the nose or throat.

Ozone, like any other substance, when taken in overdose, does irritate and is harmful, but so does oxygen if not properly diluted by nitrogen, and so do all medicaments. Just imagine the result if a druggist should multiply the figures of the doctor's prescription by 100!

We do not believe all the very sanguine statements of French doctors about the wonders of ozone in therapeutics, neither do we feel sympathy for doctors that condemn ozone on false grounds, but we think the question of enough importance for some institute to take the matter up and investigate it impartially. Until the time comes when this is done, it is better for those interested in the fate of ozone to keep quiet and hope for the best.

There will come a time when ozone will be recognized as a boon to mankind as regards therapeutic aid, or that it will be condemned as such. Seen from the industrial standpoint, it will make very little difference because the great importance of ozone in other lines gives us plenty of work, both scientific research and commercial application.

There is one application of ozone that we wish to call attention to: it is the indirect use in therapautics by the Neel-Armstrong oxyoline apparatus.

Dr. Neel, experiencing the irritating effect of ozone (unless very weak), made a device by which the ozone generated is allowed to bubble through certain etheric oils, such as eucalyptus and pine oils before being inhaled.

The company says that the gases inhaled do not contain any free ozone (no bluing of iodine starch paper at outlet).

The therapeutic value of the special products of oxidation of the oils cannot be judged by us; it is an instance of the good that may be done by ozone in an indirect way.

The company has been in the market for more than fifteen years and judging from their numerous clinical and other medical reports, oxyoline seems to be a wonderful product.

CHAPTER XVI

OZONE IN THE INDUSTRIES

WE have to be careful when reading about the applications of ozone in the chemical industries. In France there seems to have been a great deal of work done in this line, but it is rather difficult to discriminate between facts and patentee's expectations and hopes.

De la Coux devotes some 200 pages in his book to various applications or alleged applications of ozone, besides that of the purification of water; most of the statements, however, give the impression of being dreams or a work of fantasy.

The author of that book is a chemical engineer; his sayings on electricity and his criticisms of ozonators show a remarkable lack of understanding, and that makes us feel uneasy about his other statements. Chemical reactions that go on the paper as formulæ do not always happen in reality, or even if they do it is not always profitable to have them go that way. For instance $6HCl + O_3 = 3H_2O + 3Cl_2$, but there are cheaper methods than this of making chlorine.

If we say $S + O_3 + H_2O = H_2SO_4$, or $H_2S + 2O_3 = H_2SO_4 + O_2$, or $NH_3 + O_3 = HNO_3 + H_2$, these reactions, possible on paper, are not very likely to occur, and even if they did, it is not probable that anybody would apply them.

Take for example, the sulphuric-acid reaction, it would take 48 kilograms of ozone to produce 98 kilograms of sulphuric acid; the cost of the former is about double the price of the latter!

We must not look that way for applications of ozone.

There is more room for it in organic chemistry if we think of expensive or special products.

The manufacture of iodoform may be expressed by the equation:

$$3CH_3OH + 9KI + 2O_3 = 3CHI_3 + 9KOH,$$

174
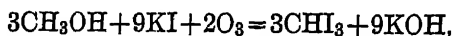
but if it reacts that way it has to be proved. It is a long time ago that in chemistry we considered the sign of equality to represent the truth; we now know that equilibrium reactions are by far the most common—perhaps all reactions are equilibrium reactions.

De la Coux enumerates a large number of reactions. Turpentine and ozone give camphor; benzene and ozone yield ozobenzene; methyl- and ethyl-alcohol and ozone give respectively formic and acetic acid; ether and ozone give peroxide of hydrogen, acetic acid, aldehyde and carbonic acid; glycerine and ozone yield the aldehyde glyceride, glyceric acid, mesoxalic, formic and acetic acids and so on, but the fewer we believe of these the better.

From an industrial standpoint it is not the question *if* but *how* a reaction goes; of course we do not intend to·say that there is nothing in these reactions that may be partially true, but we should be very · careful in accepting statements that are not supported either by authority or by actual experiment.

Keeping in mind the relatively high price of ozone it is probable that the field of organic industrial chemistry will offer more opportunities for it than the inorganic; it may even be that it is being used to a far greater extent than we know because it is an easy matter to keep a secret, and we are used to having a lot of mystery surround industrial chemistry.

In his book de la Coux gives another long list of profitable applications of ozone. The preservation of meat and milk, the aging of wines, the purification of brandies and such liquors, the manufacture of acetic acid, the treatment of beer, the bleaching of textile products, of wax, ivory, feathers, dextrines, starch, the treatment of oils, greases, soap, the manufacture of varnishes and perfumes, the aging of wood for violins and pianos, etc., etc.

Of this long list very few have actually met with success, which does not mean that now that ozone can be had in any quantity and for a reasonable price, some of those applications may not be carried out again in the near future.

The trouble is that de la Coux makes such a curious mixture of truth and fiction in his book, that one feels very skeptical when reading it, and rather than for the sake of apparent completeness accept and publish doubtful information, we shall

confine ourselves to the discussion of those applications that have been subjected to our personal experience.

One of the properties of ozone that can be made use of in the industries is its bleaching power, and here it comes in direct competition with the old-established way of bleaching by chlorine.

The advantage of ozone over chlorine as a bleaching agent is not in its price, but in its mode of application, which allows of a very evenly bleached product.

We have been treating paper pulp with ozone and obtained complete success as far as quality goes, the difference between the chlorine-bleached and the ozone-bleached product being that the fibers in the latter case were very much longer than in the former.

The length of the individual fiber is of much importance in the product because that determines the quantity of filling material that can be used to make paper from it.

For the effective bleaching and preparation of paper pulp by ozone, two things are essential—a weak concentration of ozone and a long time of contact. One of the difficulties of the application of ozone is the necessity of devising some proper method for every special case so as to carry on the process in the most economical way.

Those who are not familiar with ozone and its special features are apt to make mistakes in this line, and this is why so many trials have proved failures. It was not because the ozone did not do the work but because the experimenter, not being familiar with the subject, tried his experiment in a wrong way.

We must emphasize this point because, simple as it looks, it is not always so very simple to know the right way of application and it is an injustice to blame ozone for what it cannot help.

The faulty treatment of paper pulp with ozone is one instance that we happen to know of and there are more like it.

Another successful trial has been the bleaching and treatment of starch, whereas the bleaching of flour turned out a complete failure, the taste being strangely affected.

It may be added that the starch, a potato product, was treated in suspension in water while the flour of course had to be treated in the dry state. Ozone has very little, if any, effect when the substance to be treated is in the dry state.

It is highly probable that the prolonged action of ozone, and in stronger doses, will have a decided influence on the solubility of the starch and on its properties of " thin-boiling."

It is said that the treatment of flour will be a success if nitric oxide is introduced at the same time as the ozone. We never tried that. The bleaching of fabrics is another delicate question; in the Chemical News of 1912, p. 116, it is said that cellulose is destroyed by ozone, now fortunately it is also said that the concentration of the ozone employed was 1 or 2 per cent, expressed in the usual terms that is over 26 gm. per cubic meter !

Let us first consider the probability that where percentages are quoted, grams are meant; it is a common mistake, through ignorance of the man who copies; so let us not take this ridiculous figure of 26, but let us be wise and take 1 to 2 gm., instead of per cent; now even that is far too much for delicate materials. It is a fact that we can destroy textiles with ozone just as well as with chlorine, but the advantage of ozone bleach over chlorine bleach lies in the possibility of applying a very weak concentration of the former, more in the neighborhood of 0.1 gm. than of 1 gm.

Different textiles call for different strengths. One of the secrets of successful treatment is not to hurry the process.

Wax has been successfully bleached with ozone, but it is a tedious process unless carried out in a special way. The bleaching of oils is a difficult problem, the treatment with ozone not being advantageous unless the product can be sold for a good price.

For example, we have been treating sandalwood-oil with great success; the color was improved and above all, the bad taste was removed, which affects its selling price. It is very probable that many of the more costly oils will find a good friend in ozone.

The bleaching of linseed-oil had been carried out with complete success, the treated product being nearly colorless; but let us add here that it is of much importance to know the right way to perform the operation in order to have an even product, and not obtain varnish. The secret of success lies in details, but everybody familiar with chemical industry knows that details very often may be of primary importance.

We have no personal experience regarding the effect of

ozone on ivory, furs, and feathers, but are told that it is all that can be desired.

The bleaching of dextrine and glue resulted in a failure in that while the discoloration disappeared, the adhesive property was gone also.

It is difficult to say exactly what that " adhesive " property of some materials is. In this case we did not try to find out just what had happened; such problems generally take far more time than is usually at one's disposal, and the common fate of many experiments is, that when the first trials do not give reasons to hope for good results, they are generally left at this point.

In the history of chemical industry or rather of industrial chemistry, there are a great many instances of former failures subsequently changed to successes, and so if we now say that one cannot succeed in improving this or that property of a substance, it may be likely that after a while we shall have to withdraw that statement. It is probable that ozone will be able to improve the color of gelatine, but there is the same danger of affecting the other properties, especially adhesiveness. We were successful in bleaching albumin taken from blood, so as to make a substitute for the white of eggs, for bakeries, etc.

We have no faith whatever in the treatment of wine with ozone; wine has far too delicate a taste and, moreover, is so easily turned sour that it can hardly be possible that the alleged improvement is a fact; neither do we believe in the possibility of removing fusel oils from spirits or aging brandies and such like by ozone; it sounds very incredible. We did not succeed in bleaching tobacco leaves, but did not attempt to solve this problem but very superficially.

Quite another line of application is, not the bleaching end, but the manufacturing end. It is a well-known fact that the manufacture of vanillin from isoeugenol has been carried out on a large scale both in America and in France, and if we think of the possibilities for ozone in the organic chemical industry there is no end to it, one of the most appealing instances of its application being the industry of the coal-tar products, the dye-stuffs, perfumes, tannery, etc.

A successful application of ozone is that where it is required to make a perfectly transparent varnish out of linseed oil. How

this is done is a trade secret; the product is remarkable for its quality.

If we were to enumerate all the possible or even only all the probable successful applications of ozone in the chemical industries, this book would never come to an end, but as said before the extreme importance of the treatment of water, and the vast amount of work connected with this problem has not left us very much time to go to any depth into other applications; some of them we touched, and those have been mentioned for the greater part, others are being investigated and are not complete enough for publication.

A possible large field is the use in the rubber industry both for making artificial rubber and for renovation of old rubber.

Among the possible applications of ozone we may mention that for the treatment of effluents from factories.

Years ago, when the price of ozone was much higher, such a proposition would not have had the slightest chance. Now it has the advantages over chlorine in the simple mode of application, the absolute certainty of results and a better product as far as the quality of the water which ultimately returns to the stream is concerned. Fish object to chlorine, but are very fond of oxygen.

At the 1911 American Leather Chemists Association convention, Alsop related his experience in the line of treating tannery effluents with ozone and spoke very favorably of it.

That ozone will do the work is beyond question. It is only the cost that has to be considered.

Alsop says that the cost in no case will be higher than ten cents per thousand gallons of effluent, all expenses included.

From the description he gives of the way of applying the ozone we get the conviction that, had it been done in a more efficient apparatus it would have cost much less ozone. It seems to us that this figure could easily be reduced by half.

For those who are interested in fishery matters, it will be interesting to learn that when we had our experimental plant near a little river in Holland and had the ozonized water run into this, fish crowded in schools in front of our water outlet; of course this water was overcharged with oxygen and contained some ozone as well. All fish seemed to like this particularly well and so much the more as the water of the river was a very

bad one, so bad even (lack of oxygen) that before we were there, there were hardly any fish at all in it. For a fishery it might prove a valuable help to draw the fish toward the nets.

There may be a field for ozone in the treatment of sewage after it has been freed of all the matter in suspension.

A very simple and effective method of accomplishing a perfect clarification is to add some iron sulphate and after that some limewater; the heavy precipitate of iron hydroxides will carry down all matter in suspension and vegetable life but of course will leave many bacteria untouched.

The perfectly clear water is still more dangerous than before, because most people judge a water by its clearness.

Now ozone should come in to destroy the bacteria and the excess of iron in solution and the result will be a perfectly safe water, free from pathogenic germs or other deleterious matter.

In this special case the ozone treatment is supplementary to the removal of matter in suspension; the present low cost of ozone puts this scheme of sewage treatment on a commercial basis.

When at the Neel-Armstrong laboratory in Akron the author was shown the results of the treatment of wheat and corn by ozone, the object being to destroy moulds and such like, which cause great trouble in the storage and necessitate repeated turning over of the heaps.

The ozone-treated material proved to be entirely free from moulds and to be of a better color, and it is to be expected that this method will prove a great boon to wheat and corn and similar storage.

The treatment is very simple and inexpensive and certainly will find application.

In recapitulation of Part III we would like to quote Molinari where he says: "The last word on the applications of ozone has not yet been said but the future will perhaps bring surprises. The actual cost is not of serious moment for industrial processes yielding products of great value."

For the present moment the use of ozone is limited to that for the sterilization of drinking water and that for the purification of air in ventilating schemes; the application of ozone in

the industries is very rare, except for the part that is kept a secret.

The sterilization of drinking water is a complete success in Europe, thanks to the enterprise and skill of two firms;[1] it will be the same over here *if* and *when* a great firm undertakes the task of pioneering.

In conclusion we wish to remark that nowadays ozone can be had in any quantity and any quality—if quality stands for concentration—up to say 20 or 30 gm. per cubic meter, on a commercial basis. None of the present applications ask for such a high concentration, something like 5 gm. per cubic meter being quite sufficient for the present purposes, except perhaps the manufacture of artificial rubber, which is in its infancy yet.

For water sterilization a concentration of 1 gm. per cubic meter suits the purpose when the sterilization is carried out in the proper way and in the right apparatus. This concentration is high enough for most of the other applications.

It is a common mistake to believe in highly concentrated ozone for ordinary purposes, many a trial turned out a failure only because of the too high concentration of the ozone, its beauty lying more especially in its extreme power at low concentration.

For ventilating purposes and therapeutic applications the ozone should be very weak indeed—not a question of grams but of milligrams per cubic meter of air.

For reference we conclude this work with a list of American patents of ozonators and a list of some of the more important papers and works on ozone and discharges.[2] Most of the papers contain quite a number of references again, so that many details can be traced back to their origin.

I also wish to say that during the fifteen years of research I have had the help of Dr. F. L. Ortt, Dr. Nieuwenhuysen Kruseman, Dr. A. Lebret and Dr. H. J. van 't Hoff; their valuable advice and vast knowledge certainly have aided me a great deal in the overcoming of encountered obstacles.

New York, March, 1914.

1. Siemens & Halske of Berlin and Compagnie Générale de l'Ozone, (Otto) of Paris.
2. All of these have been consulted by the author.

PART IV

LIST OF UNITED STATES PATENTS BEARING ON OZONE

Dunderdale	1870	109,601	Miller-Ashley	1903	742,341
Dunderdale	1870	100,736	Blackman-Wilford	1903	743,431
Yost	1882	254,424	Blackman-Wilford	1903	743,432
Hill	1883	282,190	Otto	1903	744,096
Brin	1887	361,923	Wessels	1904	751,886
Merkel	1889	397,992	Wessels	1904	753,886
Verley	1889	397,517	Vosmaer	1904	754,261
de Vars	1889	409,903	Fridberg	1905	782,021
Kennedy	1890	430,387	Sahlstroem	1905	788,557
Grumbacker	1892	470,425	Otto	1905	790,655
Sharp	1892	481,676	Wood	1905	804,291
Froehlich	1892	487,390	Rice	1905	807,964
Fahrig	1893	511,330	Birtman	1906	811,364
Andreoli	1894	512,265	de Mare	1906	820,656
Donovan-Gardner	1894	527,326	Otto	1906	828,387
Andreoli	1896	565,952	Dechaux	1906	830,975
Tesla	1896	568,177	Bridge	1906	832,767
Pridham	1896	574,314	Bridge	1907	850,416
Anderson-Ditrich	1897	577,523	Potter	1907	854,965
Andreoli	1897	577,636	Ward	1907	871,652
Yarnold	1897	580,244	Beckwitt	1908	881,533
Schneller-Sleen	1897	587,770	Wood	1908	882,509
Irving	1898	596,936	Wood	1908	882,510
Otto	1898	599,455	Schneller	1908	886,874
Andreoli	1898	607,007	Elner	1908	887,155
Ramager	1898	614,500	Craig	1908	893,818
Abraham-Marmier	1898	632,391	Steynis	1908	897,318
Vosmaer	1898	636,304	Quain	1908	898,506
Tindal	1899	636,868	Kintner	1908	902,965
Otto	1900	640,694	Potter	1908	905,361
Armstrong-Neel	1900	642,663	Steynis	1908	906,468
Lamphry	1900	648,764	Steynis	1908	906,081
Elworthy	1900	653,078	Lohman	1909	919,445
Smith	1902	656,657	Vosmaer	1909	919,403
Otto	1902	707,797	Kolle	1909	909,309
Vosmaer	1902	709,427	Lohman	1909	919,445
Vosmaer	1902	709,379	Smith	1909	921,903
Curtis	1903	727,101	Kintnere	1909	920,965
Otto	1903	733,674	Friedlander	1909	927,519

Steynis	1909	924,592	Leggett	1911	1,010,777
Place	1909	932,898	Shepherd	1911	1,011,503
Bridge	1909	935,457	Fuss	1911	1,017,258
Ashley	1909	942,046	Stuart-Thompson	1912	1,024,533
Cottrell	1910	945,917	Bradley	1912	1,028,857
Rice	1910	950,347	Steynis	1912	1,035,489
Linder	1910	951,443	Leggett	1912	1,037,500
Bradley	1910	971,244	Held	1912	1,038,130
Ashley	1910	951,789	Beck	1912	1,040,123
Steynis	1910	954,597	Peek	1912	1,041,340
Lohman	1910	955,818	Bradley	1912	1,041,421
Linder	1910	969,547	Small-Linder	1912	1,044,700
Henny	1910	974,789	Spaulding	1913	1,049,775
Schaffner	1910	977,335	Walden	1913	1,050,260
Schaffner-Hutton	1910	977,336	Held	1913	1,056,789
Small	1910	978,786	Wallace	1913	1,059,014
Glaser	1911	982,227	v. Patten	1913	1,060,651
Gerard	1911	982,581	Spaulding	1913	1,060,957
Knips	1911	983,607	Hopkins	1913	1,062,974
Twombly	1911	984,722	Smith-Hummel	1913	1,063,167
Meeker-Wallace	1911	986,194	Franklin	1913	1,064,064
Meeker	1911	987,902	Franklin	1913	1,064,065
Armstrong	1911	991,767	Freet	1913	1,066,484
Patin	1911	992,980	Hopkins	1913	1,066,974
Goldberg	1911	995,958	Spurge	1913	1,071,476
Bradley	1911	996,561	Dumars	1913	1,073,106
Guilly	1911	996,850	Richards	1913	1,074,462
Steynis	1911	997,339	Steynis	1913	1,066,674
Woiland	1911	999,294			

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THIS bibliography is far from being complete; it contains about one-fifth of the total literature on the subjects, judged from the number of articles quoted in some of the literature given below. The author selected these because he has gone through all of them, mostly in the original, and the more he read about the subject the more he got the conviction that it was of little use to go to the trouble and waste of time of reading everything that has been published.

As will have been noticed when reading this book, several authors have been quoted and the quotation certified by giving the page number. Among the list given below there are many contributions that do not contain any new statement or thought; some are merely descriptions or repetitions.

It is often difficult to distinguish between appearances and realities and the greatest caution should be exercised in accepting on second-hand evidence facts which have not been verified—this certainly holds for ozone and ozone work.

It goes without saying that Science Abstracts and Chemical Abstracts both enable one to look up literature concerning ozone and its applications. Leading periodicals contain articles on ozone on different occasions. It has been found impossible to quote all of them, there being too many.

The author is fully aware of the fact that there will be many publications on ozone and related subjects that he has not seen, but believes that the more important have been read.

The order of the list is chronological.

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